Encapsulation and stabilisation of copper-chromium-arsenic (CCA) sludge from timber treatment plants

by

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DECLARATION

Except where indicated otherwise this thesis is my own work

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Abstract

Cu-Cr-As (CCA) sludges from timber treatment plants and synthetic sludge which was manufactured in the laboratory were treated using cement-based stabilisation/solidification (s/s) process. The stability of these sludges solidified within cement-sand matrices was tested using the standard regulatory method for assessing the leachability of solid waste prior to its disposal by landfill, the Toxicity Characteristic Leaching Procedure (TCLP test). During the test the samples were leached using an acetic solution for 18 hours. The regulatory acceptable concentrations of Cu, Cr and As in the leachate according to the Environmental Protection Authority (EPA) standards are 5 mg/L, 5 mg/L and 100 mg/L respectively. Although there is no regulatory requirements for structural strength of solid waste prior to its disposal in Australia, the effect of metal addition on unconfined compressive strength of cement-sand matrices was examined.

Cement-sand matrices which contained sludge manufactured in the laboratory or from the Narangba treatment plant showed little loss of metals after leaching. All of the s/s samples containing As in the concentration range 1800 to 41200 mg/kg, (chromium and copper were in the range of 910 to 25800 mg/kg and 390 to 5500 mg/kg respectively) had a concentration of As in the leachate of below 1 mg/L. The Narangba sludge and synthetic sludge were atypical sludges, since they were practically free of soluble CCA compounds. The major components of these sludges were chromium and copper arsenates which are sparingly soluble in water. When stabilised by cement they are stable in the TCLP acetic solutions and may not be considered hazardous to the environment.

It was found that the leaching of metals from cement-sand matrices was dependent on the concentration of water-soluble chromium and arsenic present in the sludges. The sludges from commercial treatment plants contained water-soluble arsenic and chromium in the range of 47 - 904 mg/kg and 35 - 1294 mg/kg respectively. In order to reduce the concentration of water-soluble metals and convert them into insoluble chromium and copper arsenates, some of the sludges were pretreated by the addition of sawdust as a reducing agent. The addition of 10 % hardwood sawdust to sludge from the Mogo treatment plant reduced the concentration of water-soluble arsenic 7-fold and chromium 117-fold. The s/s treated sludges from the Mogo treatment plant without the addition of sawdust did not pass the TCLP test. However, all of the sludges which were pretreated by sawdust met the EPA standards for disposal by landfill. Although the loadings of As and Cr in the s/s processed waste were up to 60130 mg/kg and 25000 mg/kg respectively, the concentration of As and Cr in the leachates was under 5 mg/L.

The concentration of Cr in the leachates from s/s sludge was proportional to the water-soluble chromium (VI) in the sludges. The amount of chromium in the leachates of Cr(III)-bearing cement-sand matrices was 550 times less than the amount of Cr(III) which was originally added to the mix. Cement-sand matrices were able to reduce Cr(VI) leachability less than 2-fold. Cr(VI) is probably retained in the pores of the concrete particles. Thus, Cr(VI) was not chemically stabilised but physically encapsulated. A calculation formula for predicting the concentration of Cr in the leachates has been suggested. It was found that the leaching results fitted satisfactorily with those calculated using the formula. The addition of chromium did not significantly affect the setting and hydration of cement.

Copper concentration in the leachates was 3000 times less than the theoretical leaching based on the addition of copper sulphate to cement-sand mixes. Chemical stabilisation rather then physical encapsulation was probably responsible for this reduction of copper mobility. Water-soluble copper might be stabilised by adsorption on cement or by the formation of copper hydroxide. The concentration of Cu in the most stabilised sludges was less than 1 mg/L. Cu in the form of $CuSO_4.5H_2O$ significantly retards the hydration of cement and reduces the unconfined compressive strength of cement-sand matrices.

Arsenic trioxide (III) and As_2O_5 were stabilised by cement-sand mixes consisting of 1 part of cement and 2 parts of sand. These mixes released only around 1% of As present in the s/s form and the concentration of arsenic in all of the leachates was less than 1 mg/L. Arsenic(V) in the form of As_2O_5 in pure cement inhibited hydration. The contaminated cement-sand mix hardened after two days of curing, but had substantially reduced unconfined compressive strength. The unconfined compressive strength of cement-sand matrices containing 2 parts of As(V) in the form of As_2O_5 per 100 parts of cement and 200 parts of sand was 60 N/cm^2. Although As(III) affected the morphology of cement, the unconfined compressive strength of As(III)-bearing cement-sand matrix was relatively high (990 N/cm^2).

Since water-soluble CCA compounds are of utmost importance to the environmental stability of the solidified sludges as the findings of this study clearly demonstrated, any proposed disposal method should include measures for reduction of these soluble compounds. In addition, any changes to the design of timber treatment plants should also take into consideration these findings.

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Chapter 1. Introduction

Copper-chromium-arsenic (CCA) preservatives are among the most important types of wood preservatives (Hartford, 1973; Pizzi *et al.*, 1984) and although a few problems are encountered in their industrial use they generally perform satisfactorily. One of the most important industrial problems with CCA preservatives is the formation of sludges during wood treatment operations. Sludge formation causes the following problems: delays caused by maintenance; loss of useable preservatives; and accumulation of sludges in work tanks (Pizzi *et al.*, 1984).

Sludge formation decreases the efficiency and effectiveness of treatment plants as well as reducing their economic performance. In order to minimise sludge formation it is necessary to have an insight into the chemical interactions of CCA with wood during treatment and to examine the chemical composition of sludges and the causes and mechanisms of their formation. As sludge is a hazardous waste, there has been increasing interest in minimising sludge formation in treatment plants as well as using stabilisation/solidification techniques for its safe disposal.

1.1. Objective and scope

The major objective of this thesis was to examine the chemical composition of CCA sludges and methods of stabilising them in cement to ensure that they meet current guidelines for the safe disposal of toxic waste. CCA sludges are mostly composed of chromium arsenates and copper arsenates. Other components of sludges from commercial treatment plants are sawdust and soil particles. As the treatment processes, wood species and CCA concentrations vary from plant to plant the concentrations of the components of sludges may be different. Differences in the composition of sludges might be important if toxic components are to be immobilised in an environmentally safe manner.

Cement-based methods of stabilisation/solidification have been used for the disposal of CCA sludges. Concrete matrices containing up to 11500 mg of As per kg and 16000 mg of Cr per kg have shown limited leachability of these metals, but other sludges also treated by similar solidification/stabilisation methods released up to 14 mg/L of As and 150 mg/L of Cr to the leachate (Conner, 1990). Generally, Conner's work did not clarify the effect of the composition of sludge on metal mobility.

The acceptance criteria for waste disposal by landfill according to the Environmental Protection Authority of NSW are the concentrations of heavy metals in the leachate of the waste subjected to the Toxicity Characteristic Leaching (TCLP) test. The acceptable concentration for As and Cr is 5 mg/L. These concentrations were derived from the standard for drinking water, but are 100 times in excess of the metal concentration regarded as safe for drinking water.

In this study the leachability of metals from cement-sand matrices was assessed with regard to the composition of CCA sludge and the cement-sand mix. The environmental stability of stabilised samples was assessed by leaching them in dilute acetic acid of pH 2.8 for 18h (the TCLP test) and then examining the concentration of metals in the leachate. The effect of the addition of sludges on the mechanical strength of cement-sand mixes was also investigated by measuring the compressive strength of samples. To assess the effect of some components of sludge on chemical stability and mechanical strength, cement-sand mixes containing pure As, Cr and Cu compounds were tested. The changes in the microstructure of these samples and also the effect of adding As, Cr and Cu on the hydration of cement were investigated by Scanning Electron Microscopy (SEM).

Some sludges were quite difficult to stabilise directly; therefore they were sometimes pretreated using sawdust. Sawdust acts as a reducing agent and its effect on sludges was to reduce soluble Cr(VI) to Cr(III). Since the reduction of Cr results in the precipitation

of insoluble chromium arsenates, soluble As compounds present in sludges, which may have a detrimental effect on the environmental stability of concrete matrices, are also reduced by the formation of these arsenates. The effect of the addition of sawdust on the immobilisation of metals in cement-sand matrix was thus elucidated.

1.2. Study outline

The following section (Chapter 2) reviews the relevant literature on the mechanism of CCA fixation in timber, formation of sludge, effect of treatment procedures on sludge formation, solidification/stabilisation methods for the immobilisation of the components of sludge and the test methods for characterisation of immobilised wastes prior to disposal by landfill. As the character of sludges is paramount to the quality of treated waste, Chapter 3 outlines the methods and results for the characterisation of sludges from various commercial treatment plants. Chapter 4 examines the stabilisation/solidification of chemically pure sludges. The TCLP test was the most important method used to assess the environmental stability of cement-based forms. Also in the Chapter 4, the effect of CCA sludge on the structure of cement-sand mixes was investigated using compressive strength measurements and SEM. Chapter 5 examines the stabilisation/solidification of sludges from commercial treatment plants. Finally, Chapter 6 discusses the results of the study, the effect of pretreating sludge with sawdust on the leachability of metals from cement-sand forms, and the effect of Cu, Cr and As compounds on the stability of s/s sludge. Chapter 7 presents the conclusions of the study and the recommendations for future development of CCA sludge treatment methods.

Chapter 2. Literature review

2.1. CCA formulation and fixation reactions in timber

A number of CCA formulations have been developed to reduce preservative cost and minimise preservative leachability from wood. They differ mainly in the compositions of single constituents or their relative proportions. The chemistry of the interaction of CCA preservatives and wood has been described by Pizzi (1981, 1982a, 1982b) and Dahlgren (1972). The fixation of CCA solutions in timber is a complicated process involving proton-consuming and proton-liberating reactions (Dahlgren, 1972). During treatment CCA solutions are subjected to partial reduction by organic wood compounds and show increases in pH, the precipitation of colloidal substances and later the formation of insoluble metal complexes.

The kinetics of fixation of CCA preservatives with either model compounds such as D(+) glucose, alpha-cellulose, guaiacol, lignosulphonate and wood flour from various species was examined by Pizzi (1981, 1982a, 1982b). The model compounds were chosen to avoid the problems encountered when examining whole wood which is a heterogeneous materials and hence not suitable for carrying out precise, reproducible observations. The reaction systems, CrO_3, As_2O_5, $CuSO_4.5H_2O$, and the reducing agents D(+) glucose, alpha-cellulose, lignin, guaiacol and wood, were monitored for different times at various temperatures. To obtain reaction characteristics the optical properties of Cr(III), Cr(VI), As and Cu ions in the UV/Vis spectrum were examined. Changes in pH were also monitored and the elemental composition of precipitates was examined using atomic absorption spectroscopy (AAS).

From the results of these studies the authors concluded that chromium reacts with cellulose in two stages. Initially adsorption of Cr(VI) by cellulose followed by reduction to Cr(III). Chromium may also react with lignin and it was suggested that the

reaction of Cr(VI) with lignin involved three successive reactions of $Cr_2O_7^{2-}$, $HCrO_4^{2-}$, and CrO_4^{2-} to form insoluble Cr(VI)/guaiacyl lignin complexes.

However, a more recent study of the reaction of guaiacol with chromic acid has discounted Pizzi's suggestion that guaiacol is cross-linked by hexavalent chromium species. It was considered more likely that the major product of the reaction of Cr(VI) with guaiacol are oxidised guaiacol oligomers which are tightly held in polymeric complexes, bound or cross-linked by hydroxylated trivalent and presumably octahedral chromium species (Schmalzl *et al.*, 1995).

The total reaction of CCA solutions with wood components was schematically interpreted as involving three successive reaction phases (Pizzi 1981, 1982a, 1982b): In the first phase Cr(VI) is chemically adsorbed by cellulose and $Cr_2O_7^{2-}$ reacts with lignin guaiacyl units to form complexes. At this stage the increase in the pH of the system with time is fairly slow. In the second phase, the fast reaction of $HCrO_4^-$ with lignin takes place to form insoluble polymeric complexes. A rapid increase in pH accompanies this reaction. The third phase is determined by the reduction of Cr(VI) to Cr(III) on cellulose sites. During this stage the pH shows a modest rate of increase. Most of the Cr(III) remains weakly bound to cellulose, but some Cr(III) is released to the treatment solution.

Hartford (1986) has suggested that the reduction of Cr(VI) during fixation of CCA preservatives occurs in several reaction steps.

$$2\ Cr_2O_7^{2-} + 3\ CH_2O + 16\ H^+ \Rightarrow\ 4\ Cr^{3+} + 3\ CO_2 + 11\ H_2O \qquad [1]$$

This reaction consumes hydrogen ions, and Dahlgren (1972) observed that the pH of treatment solutions in contact with wood increases with time to pH 5.5, which is the

normal pH of wood. At this pH, the following precipitation reactions take place :

$$Cr^{3+} + H_2AsO_4^- \Rightarrow CrAsO_4 + 2\ H^+ \quad [2]$$

$$2\ Cu^{2+} + H_2AsO_4^- + H_2O \Rightarrow Cu_2(OH)(AsO_4) + 3\ H^+ \quad [3]$$

$$8\ Cr^{3+} + Cr_2O_7^{2+} + 11H_2O \Rightarrow 2\ Cr_5O_9 + 22\ H^+ \quad [4]$$

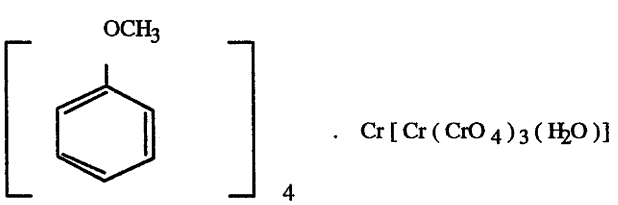
$$4\ Cr_5O_9 + 4\ CH_2O + O_2 \Rightarrow 10\ Cr_2O_3 + 4\ CO_2 + 4\ H_2O \quad [5]$$

Reaction [2] was observed by McMahon *et al.* (1942) when CCA solutions were reduced by glucose in vitro. It has been suggested that reaction [3] results in the formation of the crystalline mineral olivenite, $Cu_2(OH)(AsO_4)$ (Hartford, 1986). Oxidation to Cr_5O_9, which is the result of the fourth reaction, probably only occurs on the surface of wood (Hartford, 1986).

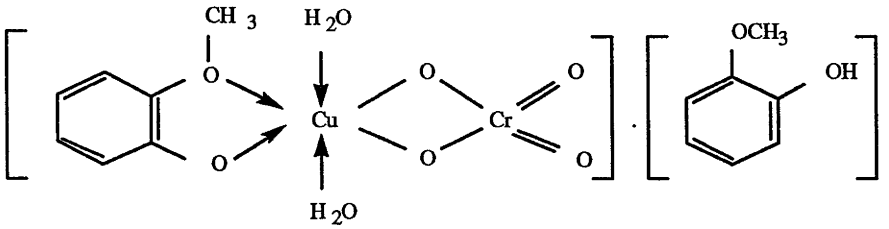
It is probable that the reduction of Cr(VI) to Cr(III) in treatment solutions containing Cu and As is responsible for the formation of sludge. The presence of arsenic has a strong influence on the production of Cr(III) and reduces the duration of the second reaction phase (Pizzi, 1982b). A similar effect has been found in the presence of Cu(II). The reactions in the second phase are considerably faster and are associated with a steeper pH increase (Pizzi, 1982b).

A wide spectrum of chemical species can be formed during the reaction of CCA solutions with wood. In the case of the reaction of CrO_3 with guaiacol/glucose it has been suggested (Pizzi, 1981) that the substance formed is a $Cr[Cr(CrO_4)_3(H_2O)]$ .4[guaiacol units] complex .

The structural formula of this compound is:



At the end of the second phase $\{[H_2Cr_2O_7]_2[guaiacyl\}_2\}_n$ is a major complex which forms around 80% of the total Cr bound onto lignin (Pizzi, 1981). In the presence of copper, both Cu and Cr may participate in forming a Cu/Cr guaiacol complex with the following structural formula (Pizzi, 1982 a).



Again more recent work (Schmalzl *et al.*, 1995) on the reaction products of chromic acid with guaiacol have suggested that different chemical species to those observed by Pizzi may be found. Thus it was observed that the reaction of chromic acid with guaiacol forms the symmetrical carbon-carbon coupled dimer 3,3'-dimethoxy-[1,1'-biphenyl]-4,4'-diol, the trimer 3,3",5'-trimethoxy-[1,1':3'1"-terphenyl]-4,4',4"-triol, 4,4'-dipheno-quinone, 2-methoxy-p-benzoquinone and an inert highly soluble polymer consisting of guaiacol oligomers bound or crosslinked by hydroxylated trivalent chromium species.

A considerable amount of copper does not react with chromium. The portion of copper which is likely to be complexed by guaiacol will remain in solution in model compound systems. In wood there are indications that Cu and Cr are mainly bound to lignin. The following scheme illustrates the reactions of copper and chromium with guaiacol.

$Cu + CrO_3 + lignin \Rightarrow$

- guaiacyl-$CuCrO_4$-guaiacyl
- guaiacyl-Cu^{2+} + CrO_4^{2-}-guaiacyl
- guaiacyl-Cu^{2+}
- guaiacyl.$HCrO_4^{2-}$; guaiacyl.CrO_4^{2-}; guaiacyl.$Cr_2O_7^{2-}$
- (guaiacyl $HCrO_4^-$)n: (guaiacyl CrO_4^{2-})n
  (guaiacyl $Cr_2O_7^{2-}$)n
- guaiacyl-($CuCrO_4$)
- guaiacyl.$HCrO_4^-$.guaiacyl; guaiacyl-CrO_4^{2-}-guaiacyl;
- guaiacyl-$Cr_2O_7^{2-}$-guaiacyl;

Analysis of the reaction products of a Cr/As system with D(+) glucose (Pizzi, 1982b) showed that compounds such as $CrAsO_4.6H_2O$ occur at precipitation. Chromium arsenate can be in forms such as $Cr(OH)HAsO_4.2H_2O$ or $Cr(OH)_2.H_2AsO_4.H_2O$. In the systems discussed above, Cr(III) complexes with guaiacol have been found for the first time (Pizzi, 1982b). In this way Cr(III) seems to be mainly attached, as stable AsO_4^{3-} complexes, to the lignin of wood.

Dahlgren (1972) has suggested that the final equilibrium products of precipitation, when the pH of the treatment solution increases to 4.0-5.5, are $CrAsO_4$, $Cu(OH)CuAsO_4$ and $Cr(OH)_3$.

2.2. CCA sludge formation

Pizzi *et al.* (1984) have shown that wood is the catalyst which triggers off the sludge forming reactions in CCA solutions. If preservatives are used repeatedly during successive treatments, wood residues and wood extractives accumulate in the treatment solutions causing precipitation of sludge (Rak and Clarke, 1975).

Two different types of sludge are formed in CCA solutions. The first is formed when wood is impregnated under standard vacuum-pressure conditions at ambient temperature and within the American Wood Preservers' Association (AWPA) accepted pH and chemical composition range (Hartford, 1986), while the second is formed under extreme conditions (Pizzi *et al.*, 1984).

Temperature has the most marked effect on the stability of CCA solutions (Rak and Clarke, 1975). When treatment temperatures are increased, the amount of precipitated chromium, arsenic and copper increases (Pizzi, 1983). Similarly, in Tanalith (commercial CCA) solutions of varying arsenic concentrations (Mason, 1982), the level of sludging is significantly greater at higher temperatures. At higher CCA concentrations there is a large drop in arsenic sedimentation (Mason, 1982). Initial pH and salt concentration are t

some degree synonymous as a higher level of arsenic will produce a solution with a lower pH value. As arsenic acid is a weaker acid than chromic acid, formulations with a higher content of chromic acid will also have a lower pH. With increasing pH during treatment, reaction equilibria shift towards insoluble salts, and sludging will eventually occur.

McMahon *et al.* (1942) observed the conversion of CCA solutions into insoluble salts when the reducing agent dextrose was added to treatment solutions. This is shown by equation [6]:

$$K_2Cr_2O_7 + CuSO_4.5H_2O + As_2O_5.2H_2O + \text{reducing agent} \Rightarrow$$
$$CrAsO_4 + CuCrO_4.2CuO + Cu_3(AsO_4)_2 + Cr_2(CrO_4)_3 + Cr(OH)_3 + Cu(OH)_2 + K_2SO_4$$

The only soluble substance in these reaction products is potassium sulphate.

Analyses of CCA solutions which were in contact with wood or which were extracted from wood by vacuum revealed changes in elemental composition which may influence sludge formation. Treatment time had a crucial influence on the extent of sludging of vacuum extracted solutions. The longer the treatment time, the greater the extent of elemental depletion in the extracted solution (Pizzi *et al.*, 1984). The Cu : Cr : As molar ratio of a CCA solution just in contact with wood was 4 : 4.75 : 4, whereas the molar ratio of a solution which had been extracted by vacuum from the wood was 3.4 : 5.9 : 3.7. The original molar ratio of the CCA solution was 3 : 6 : 4. Thus, after several cycles treatment solutions may show not only depletion of active substances but also component imbalances which favour sludging (Mason, 1982).

Sludges in solution after vacuum consisted of copper chromates, chrome arsenates and copper reacted with wood carbohydrates in the molar proportions of 2.2 : 3.7 : 1.2 (William-Wynn, 1977). Sludges in solution just in contact with wood had molar proportions of 1.62 : 3.13 : 1, and 0.45 molar parts of copper arsenate.

2.2.1. Effect of process conditions at treatment plants on sludging

During full and empty cell treatments wood may be in contact with CCA solutions for approximately 2-3 hours. The sap-displacement treatment requires up to 40 hours contact between the wood and the treatment solution (Mason, 1982). During the latter process some components of the wood may leach into the preservative solution in the treatment cylinder and if present in sufficient concentrations may cause the formation of CCA sludge (Mason, 1982). In addition, since these wood components are recirculated with preservative during the treatment process, their accumulation during treatment cycles may result in excessive sludging (Pizzi, 1984). As mentioned previously sludging is more pronounced when the temperature of CCA solution is increased (Rak and Clarke, 1975). Ambient temperatures in sub-tropical regions tend to favour the generation of sludge, particularly in the front sump. The amount of sludge that forms in a plant which treats 25 000 cubic metres of radiata pine roundwood annually is about 2 tonnes (Mutandadzi, 1991). Metallic sludge is of a green colour due to Cr(III) compounds (McMahon *et al.*, 1942), but extraneous material such as sawdust and soil particles can give it a brown colour. Although the concentration of metals in such sludges is reduced, they still have to be treated prior to disposal by landfill.

2.3. Cement-based stabilisation/solidification (s/s) techniques and leach testing procedures

Once generated, CCA sludges contain toxic elements which may become hazardous to the environment. If they are not safely isolated, they may subsequently be converted into soluble toxic substances in the soil and later absorbed by living organisms (Leeper, 1978).

Presently, there are several techniques for waste immobilisation and these vary according to the chemical and physical character of the waste. Over a period of time industrial wastes have been successfully disposed of by applying solidification and

stabilisation techniques and some of these techniques might be suitable for the safe disposal of CCA.

Solidification is a process in which waste is combined with a binder to produce monolithic blocks with high structural integrity and physical characteristics thereby allowing the material to be readily handled and transported (Wiles, 1987, 1989). Stabilisation involves processes which limit the solubility of the waste and convert it into a more chemically stable or less toxic form (Wiles, 1987, 1989).

2.3.1. Operational procedures

There are usually five basic steps between the initial reception of a waste at a solidification treatment plant and final disposal (Sollars and Perry, 1989).

(a) Analysis and assessment

(b) Pretreatment

(c) Addition of binders and solidifying agents

(d) Quality control of the end product

(e) Disposal or use of the end product

2.3.2. Binders

Binders can be divided into two categories: inorganic and organic. Inorganically based stabilisation/solidification (s/s) systems include varying combinations of hydraulic cements, lime pozzolanas, gypsum, and silicates.

Organic binders include epoxy polyesters, asphalt, polyolefins (primarily polyethylene and polybutadiene), and urea-formaldehyde (Wiles, 1989). Combinations of inorganic and organic binders have been used, including polystyrene and cement, polyurethane and cement, and polymer gels with silicate and lime cements (Telles *et. al.*, 1987; Wiles, 1989).

2.3.2.1. Portland cement

Portland cement is one of the most widely used binders for inorganic wastes in s/s processes. The chemical composition of Portland cements is approximately as follows; CaO: 60-67%, SiO_2: 17-25%, Al_2O_3: 3-8%, Fe_2O_3: 0.2-6.0 %, MgO: 0.1-5.5 %, Na_20 + K_2O: 0.5-1.3 %, and SO_3: 1-3 % (Lea, 1970). The main hydration products are calcium hydroxide, hydrated calcium silicates, calcium sulphate, hydrated calcium aluminates, hydrated magnesium aluminates, hydrated calcium ferrites, and other calcium aluminoferrite and sulphoaluminate hydrates (Lea, 1970). The hydration products are dominated by the calcium silicate phases, and these provide the main source of strength during setting.

The setting time of Portland cements is generally a function of composition. The greater the proportion of alumina and ferric oxides the more rapid is the initial set. In commercial Portland cements the addition of gypsum controls the setting time.

2.3.2.2. Lime/fly ash

Another well-known system which produces cementitious reactions is lime/fly ash. Lime reacts with fine siliceous fly ash in the presence of water forming a hard, pozzolanic concrete. A typical fly ash for hazardous waste disposal contains at least 70% silicon dioxide, aluminium oxide and iron oxide. The amount of material lost on ignition must be less than 12% (Roberts, 1978). The typical chemical composition of fly ash is SiO_2: 45.7%, Al_2O_3: 26.0%, Fe_2O_3: 17.1%, CaO:3.8 %, SO_3: 2.6 %, K_2O: 1.5 %, TiO_2: 1.2 %, MgO: 1.2 %, Na_2O: 0.6 %, and P_2O_5: 0.3 % (Torrey, 1978). The performance of fly ash solidification techniques depends on fly ash particle size and its distribution (Sell, 1988). It is generally accepted that for a given ash, the finer it is, the better are the pozzolanic properties and degree of solidification.

2.3.3. Characterisation of stabilised wastes

The chemical composition of wastes is one of the most important factors affecting their solidification and stabilisation (Wiles, 1989). Small amounts of some compounds can affect the strength, durability, and permeability of Portland mixes (Jones *et al.*, 1989). Table 1 shows that even minor quantities of some chemical substances act as accelerators or retarders of the setting of cement-based binders and can cause poor performance in s/s products (Wiles, 1989).

Table 1. Effect of selected chemicals on cement-based pozzolanic processes.

Chemical	Important function					
	Flocculant	Dispersant	Matrix Disrupter	Retarder	Accelerator	Destroys reaction
Carboxylic acids		X		X		*
Carbonyls		X		X		*
Amines	X				X	*
Alcohols				X		*
Sulphonates	X			X		
Glucose				X		*
Chlor-hydrocarbon			X	X		X
Oil						>25-30%
Calcium chloride			>4%@		<2%@	>4%
Iron#	X		X		X	
Tin			X	X		
Lead			X	X		
Borates			X	X		
Magnesium	X		X	X		
Gypsum(hydrate)				X		
Gypsum(anhydrite					X	*
Silica		X			X	

* At high concentration

@ Only in certain form

Ratio of Fe(II) to Fe(III) important

Retarders have been defined as compounds which precipitate aluminates around the cement grains (Lea, 1970). They have been divided into four groups according to the type of curve obtained when initial setting time was plotted against the quantity of retarder added (Fig. 1) (Lea, 1970).

The salts falling in these groups were as follows:

1 $CaSO_4.2H_2O$, $Ca(ClO_3)_2$, $CaCl_2$

2 $CaCl_2$, $Ca(NO_3)_2$, $CaBr_2$, $CaSO_4.1/2H_2O$

3 $NaCO_3$, Na_2SiO_3

4 Na_3PO_4, $Na_2B_4O_7$, Na_3AsO_4, $Ca(CH_3COO)_2$

Fig. 1. Action of various retarders

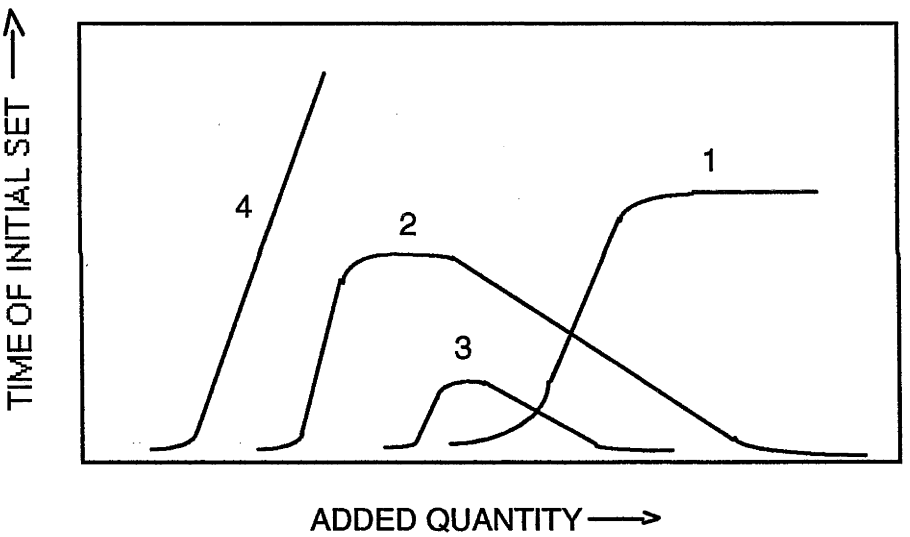


Table 1 and Fig. 1 indicate that some salts retard the setting of cement, while others accelerate it; other groups of salts retard the setting when present in small amounts and accelerate it when larger amount are added. For example, the addition of very small amounts of calcium chloride sometimes retards the setting of Portland cement, whilst the addition of larger amounts produces an acceleration. However, amounts greater than 4 percent may act as a matrix disrupter. Organic wastes containing hydroxyl and carboxyl

acid functional groups and some solvents can be expected to delay or completely inhibit cement based reactions responsible for solidification (Wiles, 1989).

Since large amounts of some constituents in waste can cause difficulties in the setting of cement, this fact must be taken into account during pretreatment procedures prior to solidification. Some pretreatment can be carried out to convert toxic components into either non-toxic or insoluble species in order to minimise the leachability of treated waste from the final s/s product. Acid or strongly alkaline waste can be neutralised by the addition of lime or acid respectively. The adjustment of pH must be a compromise to produce the lowest possible amounts of soluble ions, taking into account the concentration of substances which are present. Before a waste is subject to treatment the following properties and the concentration of some chemical species, which are shown in Table 2, are assessed (Sollars and Perry, 1989).

Table 2. Properties and chemical species which are assessed before a waste is subject to treatment

Properties	Chemical species
Appearance	Chromium
Specific Gravity	Copper
Flash Point	Iron
Total dry matter	Lead
Total inorganic solid	Nickel
Ash	Zinc
pH	Cyanide
	Sulphide

In addition to chemical effects, the physical conditions during the setting or curing process are also of considerable importance because they may influence the quality of the final product. Temperatures below 0 °C or over 66 °C will retard setting or completely destroy curing reactions, while temperatures several degrees over 30 °C will

accelerate setting (Wiles, 1989). High humidity also accelerates setting. Extensive mixing, especially after the gel-formation phase, may destroy solids and result in an extremely low strength product.

2.3.4. Assessment of product quality

During the past ten years there have been a number of strategies developed for the immobilisation of CCA sludge. These immobilisation methods mostly use various cements containing additives such as silicate and lime (Conner, 1990). Many of them are proprietary. Although a number of cement based techniques have been successfully applied to CCA disposal, there has been little published scientific research on the influence of waste components on final product quality.

2.3.4.1. Surface techniques

Poon *et al.* (1985) studied the mechanisms involved in the fixation of hazardous heavy metals such Zn and Hg in solidified mixes. X-ray diffraction (XRD), SEM, mercury intrusion porosimetry (MIP), and leaching and compressive strength tests suggested that at least two separate mechanisms were involved in the interaction between these metals and the Portland cement-silicate system. The presence of Zn affected the rate of hydration and caused the extensive growth of ettringite crystals. Leaching and MIP examinations indicated that Zn might be chemically stabilised. However, Hg remained in poro solution and was slightly bound to the hydration products through sorption. The metal was therefore mainly physically encapsulated within the cement matrix.

As the relative strength of Van der Waals' bonds, hydrogen bonds and valency bonds is of the order of 1:10:100, elements or chemical groups which are immobilised in cement matrices by chemical fixation will probably show lower leachability than those that are physically encapsulated. This will be particularly significant when a solidified block is disintegrating. Thus, the chemical compatibility of waste with the components of the

solidified systems are of particular importance for improving the chemical stability and leaching characteristics of s/s systems.

2.3.4.2. Leaching and physical testing procedures

The type of leaching test used may influence the quantity of metals leached from solidified wastes (Myers and Hill, 1986). According to the EP Tox procedure (US EPA, 1987) representative samples are considered to be composed of not less than 90% of the particles passing through a 9.5 mm mesh sieve. This sample is exposed to acetic acid at pH 5 for 24h. Tests at Koppers-Hickson Trentham (Butler, 1990) showed a large difference between particles under 9.5 mm and very fine particles. The leachate obtained from fine particles contained up to five to ten times more metals than that obtained by leaching larger particles. At present the standard regulatory leaching test for waste disposal by landfill in Australia is the Toxicity Characteristic Leaching Procedure (TCLP) (US EPA, 1986). This test is similar to the EP Tox procedure, but two acetic acid solutions of pH 2.8 and 5.0 may be employed depending on the character of waste to be tested. For alkaline wastes ~~forms with high alkaline capacity~~ such as concrete an extraction solution of pH 2.8 is usually used and crushed samples are leached for 18 h.

At present, there is still no set of standard tests for evaluating the environmental performance of solidified wastes and their intrinsic properties. Environment Canada and the US Environmental Protection Agency have conducted a study to develop a protocol of twelve methods for solidified waste characterisation (Stegemann *et al.,* 1988; 1990). The physical properties measured included water content, bulk density, solids specific gravity, unconfined compressive strength, permeability and resistance to wet/dry and freeze/thaw weathering. The chemical properties measured included acid neutralisation capacity, contaminant specification using a sequential chemical extraction procedure, equilibrium leachability using both distilled water and acetic acid as leachants, and contaminant mobility using a dynamic leaching test.

Bulk density, water content and specific gravity are physical properties which have no direct environmental significance, but they are necessary for calculating porosity and they may be correlated with other properties, such as diffusivity, permeability, and resistance to weathering.

Unconfined compressive strength is a measure of the ability of a sample to resist mechanical stresses. In Australia there are no requirements for compressive strength if the structural integrity of the solidified waste is of secondary importance in the landfill (Victoria EPA, 1986). If the solidified material requires mechanical strength, the compressive strength may be determined using the Australian Standard AS 1289 test method (Victoria EPA, 1986). Compressive tests using the American Society of Testing Materials (ASTM) C109-64 method specifies the use of 50 mm cubes (ASTM, 1987).

The compressive strength values of solidified waste using the Sealosafe treatment method developed by Leigh Interests (1988) is shown in Table 3. Hardening continues for 28 days at which time the product reaches its maximum compressive strength.

Table 3. Compressive strengths of wastes treated by Sealosafe formulations

Waste	Compressive Strength [MN/m^2]	
	After 7 days	After 28days
Arsenic waste	390	750
Chromic waste	108	220
Chromium waste	155	310

The hydraulic conductivity (or permeability) of a solidified waste determines whether ground water flow will occur through the waste body. The conductivities measured by Leigh Interests (1988) are presented in Table 4.

Table 4. Permeability coefficient of materials

Material	Coefficient of permeability [ms^{-1}]
Clean gravel	$1.\ 10^{-2}$ and greater
Clean coarse	$1.\ 10^{-2}$ - $1.\ 10^{-3}$
Sand mixture	$1.\ 10^{-4}$ - $1.\ 10^{-5}$
Fine sand	$5.\ 10^{-5}$ - $1.\ 10^{-5}$
Silty sand	$5.\ 10^{-5}$ - $1.\ 10^{-6}$
Silt	$5.\ 10^{-6}$ - $1.\ 10^{-7}$
Clay	$1.\ 10^{-9}$ and smaller
Typical concrete	$1.\ 10^{-8}$

Equilibrium extraction is used to determine which contaminants have been immobilised by solidification. The acid neutralisation capacity characterises solubility of toxic constituents under acidic conditions. The dynamic leaching test expresses the measure of the mobility of the contaminants through the solidified waste matrix.

The acceptance criteria for landfill disposal of some toxic elements by the NSW EPA using the TCLP leaching test are presented in Table 5.

Table 5. Acceptance criteria for landfill disposal

Element	Maximum concentration [mg/L]
As	5
Cr	5
Cd	1
Cu	100
Fe	100
Hg	0.1
Se	1
Pb	5

2.4. Concluding summary

This literature review has suggested that CCA sludge formation depends on the process treatment parameters at the timber plants and the sludge formation itself is related to the process of fixation of CCA preservatives in wood.

At present cement-based solidification/stabilisation treatment methods are sometimes used for the immobilisation of CCA sludge prior to disposal by landfill. However, from the available results of leaching tests (Conner, 1990) one cannot infer the effects of single or combined CCA constituents on the leachability of metals from these cement-sand matrices. In addition, it is still not clear, whether chemical stabilisation or physical encapsulation is the factor responsible for reducing the mobility of CCA sludge components in cement-sand matrices.

Since some constituents of CCA sludge can cause difficulties in the setting of cement and the immobilisation of metals this fact must be taken into account during pretreatment procedures prior to solidification. Some pretreatment may be necessary to convert toxic components into either non-toxic or insoluble species if the leachability of metals from treated waste does not meet current guidelines for their safe disposal.

Chapter 3. Characterisation of CCA sludges

Small differences in the character of CCA sludges may influence the effectiveness of solidification processes. Solidification procedures should stabilise the waste in a manner that is acceptable under current land disposal criteria and in a way that is economically acceptable. Thus, the solidification formulation should be designed in accord with the character of the sludges. Therefore prior to investigating the interaction of the principal components of CCA sludges with cement-sand mixes, sludges from a variety of treatment plants, and synthetic CCA sludge free of extraneous components was prepared and characterised. The effect of adding sawdust (a reducing agent) on the concentration of water soluble Cu, Cr and As in sludge from four commercial treatment plants was also examined.

3.1. Materials and methods

3.1.1. Preparation of synthetic CCA sludge

CCA sludge was prepared by adding ethyl alcohol to a 10% CCA treatment solution as follows: A 10% CCA solution was prepared by diluting 34% commercial CCA (Tanalith C) concentrate with water. The concentrate was thoroughly mixed and 294 mL of it was mixed with 706 mL of water in a 2 L-Erlenmeyer flask. Then 100 mL of ethyl alcohol was added. This solution was left at room temperature (20 °C) for 3 days. During this time precipitation of insoluble salts occurred. The green precipitate was then washed 5 times with distilled water and centrifuged using a Sorvall BC-5B DuPont Instruments centrifuge and dried at 105 °C in an oven. The oven-dry sludge was reduced to a powder in a porcelain mortar.

To calculate the amount of ethyl alcohol needed for the reduction of cations in solution it was considered that ethyl alcohol was completely oxidised to acetaldehyde by the CCA. In theory ethanol can also be oxidised to acetic acid. During the reaction Cr(VI) is

reduced to Cr(III). McMahon *et al.* (1942) suggested that the reaction products are compounds containing only As(V). Although it has not been confirmed that As(V) is reduced to As(III) this possibility was also considered in the calculation.

3.1.2. Characterisation of sludges from timber treatment plants

3.1.2.1. Air-dry sludge

Samples of sludge from the front sump of 7 treatment plants were dried at 20 °C on steel plates for 14 days. Samples were then placed over a desiccant (silica gel) in a desiccator for 2 days before their mass was determined. Sludge from the Hume plant which contained a lot of soil was washed 3 times in an excess of water before drying.

3.1.2.2. Oven-dry sludge

Air-dry sludge (2 g) was placed in a drying-oven (105 °C) until a constant mass was achieved. The mass of dry residue was determined and the content of physically bound water was calculated [7]:

$$WP = \frac{AS - OS}{OS} * 100 \quad [\%] \qquad [7]$$

where: WP - content of water [w/w%]

AS - weight of air-dry sludge [kg]

OS - weight of oven-dry sludge [kg]

3.1.2.3. Organic matter lost on ignition

Oven-dry sludge (2 g) was ignited in a furnace at 800 °C for 4h. The mass of the ignited residue and hence that lost on ignition was then determined [8].

$$LI = \frac{OS - IS}{OS} * 100 \quad [\%] \quad [8]$$

where: LI - lost on ignition

IS - weight of sample after ignition [kg]

3.1.2.4. pH determination of sludges

Air-dry sludge (5 g) was put into a 50 mL-beaker, 25 mL of distilled water was added and the mixture was stirred for 1h. The pH of the mixture was then measured using a digital pH meter (PHM 84) after a settling period of approximately 12h. The pH meter was calibrated using standard buffer solutions (tablets pH 4.0 - 33154, BDH Chemicals and buffer tablets pH 7.0 - 1568-00, Koch-Light).

3.1.2.5. Determination of metals

Air-dry sludge (0.5 g) was placed in a 250 mL-Erlenmeyer flask. 15 mL of 70% w/w HNO_3, (AnalaR, BDH Chemicals) and 5 mL of 70% w/w $HClO_4$, (Analytical Univar Reagent, Ajax Chemicals) was added. The flask was placed on a hot plate and the mixture was reduced to 1 mL. After cooling the reaction mixture was filtered using filter paper (No. 42) into a 250 mL-volumetric flask and diluted to the mark. The total amount of metals (Cr, Cu, As Ca, Fe K, Mg, Na) dissolved in acid were determined using a Varian, SpectrAA 20 Atomic Absorption Spectrophotometer (AAS). Although arsenic is classified chemically as a metaloid, this term may not be strictly applied if it is found in association with heavy metals such as copper and chromium. Before analysis, solutions were diluted to reduce their concentration to the optimum working range. Atomic absorption of metals were measured at specific wavelengths. Table 6 shows the standards and working wavelengths used in the analyses.

Table 6. Standards and working wavelengths for Atomic Absorption Spectroscopy

Element	Standard	Working Wavelength [nm]
As	$AsCl_3$	193.7
Ca	$CaCl_2$	422.7
Cr	$Cr(NO_3)_3$	357.9
Cu	$CuCl_2$	324.7
Fe	$FeCl_3$	248.3
K	KCl	766.5
Mg	$MgCl_2$	285.2
Na	NaCl	589.6

3.1.2.6. Determination of soluble copper, chromium and arsenic in the sludges

Fresh sludge (5 g) was placed into a 50 mL-plastic tube and 40 mL of distilled water was added. The mixture was then centrifuged for approximately 60 s and the aqueous component was separated using filter paper (No. 42). The filtrate was placed in a 100 mL-volumetric flask and acidified with 0.2 mL of 70% HNO_3. The concentration of copper, chromium and arsenic in the filtrate was determined using AAS. This procedure is similar to the method used at some commercial (Koppers) wood preservation plants for determination of unfixed CCA compounds in timber.

3.1.2.7. Determination of chlorides, sulphides and sulphates

Sludge (5 mg) was combusted in an "oxygen" flask to bring Cl and S to an ionic form. The combustion products were absorbed in 0.5% H_2O_2 solution. The pH of this solution was adjusted with several drops of saturated NaOH. The solution was then run through a separation column (filled with Silica gel 60). Chlorine in the form of chlorides and sulphur in the form of sulphides and sulphates were determined using a Dionex Ion Chromatography, Dionex QIC™ Analyser.

3.1.2.8. Determination of mono and disaccharides

Air-dry sludge (2 g) was extracted (leached) with 170.5 mL of distilled water for 2 h at 90 °C. The leachate was placed in a 200 mL-beaker and 7.5 mL of 72% w/w sulphuric acid, (AnalaR, BDH Chemicals) was added. After 4h the solution was neutralised with barium carbonate. The resulting mixture was then centrifuged in 100 mL-tubes using a MSE Multex centrifuge for 10 minutes. The supernatant was filtered using filter paper (No. 42). The filtrate was collected and reduced to dryness on a hot plate at 90 °C. The resulting residue was then redissolved in 1.0 mL of deionised water. Subsequently, 1 µL of this filtrate was injected into a Waters µm silica Radial-Pak column (100 mm in length, 8 mm internal diameter) which had been pre-treated with a 1% Silica Amine Modifier, SAM2 (Waters # 10879) in 85% acetonitrile. The flow rate was 3 mL/min for 5 h. The SAM2 was added to the water first and this solution was then added to the acetonitrile and left to equilibrate for 24h. Major sugars in the hydrolysate were detected using a Waters 401 differential refractometer and identified quantitatively using 1% sugar solutions of D-arabinose, D-xylose, D-mannose D-glucose and D-galactose run as external standards.

3.1.2.9. CCA sludges with addition of sawdust: the effect of adding sawdust on the concentration of water soluble copper, chromium and arsenic

Hardwood (*Eucalyptus fastigata*, Deane & Maiden) sawdust, used as a reducing agent was added to the Penrose and Mogo sludges at rates of 10 and 20%. Thirty or 60 % of water was then added to form aqueous mixtures with the following composition: 100 parts of sludge, 10 parts of sawdust and 30 parts of water; or 100 parts of sludge, 20 parts of sawdust and 60 parts of water. These mixtures were then placed in plastic bags, mixed thoroughly, and placed in an environment cabinet at 20 °C for 14 days. The samples were analysed for soluble copper, chromium and arsenic as follows: 5 g of the sample was mixed with 100 mL of distilled water and stirred for 5 min using a magnetic stirrer. The supernatant was then separated using filter paper (No.42). The leaching of

the sample was repeated 4 times and the combined supernatants were analysed using AAS.

3.2. Results

The concentrations of Cu, Cr and As in the synthetic sludge are given in Table 7 (results are expressed on the basis of the oven-dry weight of sludge). This chemically pure sludge was green in colour. The major components of metallic sludges are chromates, arsenates and also chromium hydroxide (McMahon *et al.*, 1942), and clearly, chromium(III) compounds give sludges their green colour. The synthetic sludge was characterised by a high concentration of As, namely 31.05 % and this accords with observations of arsenic loss in CCA solutions due to sludging (Mason, 1982, Pizzi *et al.*, 1984). However, the type of treated wood, preservative solution and treatment process can greatly influence the composition of sludge (Pizzi *et al.*, 1984).

Table 7. Concentrations of Cu, Cr and As in the synthetic sludge

Element	Synthetic sludge [w/w%]
Cu	7.42
Cr	16.07
As	31.05

The location of the commercial treatment plants from which the sludges were obtained, the type of wood treated at the plant, and the appearance of the dry sludges are given in Table 8. In contrast to the synthetic sludge, the sludges from treatment plants contained a significant amount of extraneous materials such as soil, sand, sawdust and pieces of wood. Only sludge from the Narangba treatment plant had a similar appearance to the synthetic sludge. The green colour of the latter sludge indicated a high content of chromium salts. If a significant amount of extraneous material, particularly soil, was present the sludge had a brown colour.

Table 8. Location of Koppers treatment plants from which the sludges were obtained and the type of wood treated at the plant

Sample	Location of treatment plant	Treated wood	Appearance of the sludges
1	Hume, ACT	Radiata Pine [Air Seasoned]	muddy brown, high proportion of soil and small pieces of wood
2	Grafton, NSW	Hardwoods	greenish brown, high content of sand and small stones
3	Longford, Tasmania	Hardwoods & Radiata Pine	brown, high proportion of wood and soil
4	Narangba, Queensland	Slash Pine [Steam preconditioned]	green, homogeneous with particles of organic matter, almost free of soil
5	Mogo, NSW	Hardwoods	greenish brown, high proportion of soil, sawdust and wood
6	Takura, Queensland	Slash Pine	yellow brown, high proportion of soil and sand
7	Bombala, NSW	Pine Radiata [Steam preconditioned]	brown, high content of sawdust, wood, soil
8*	Narangba, Queensland	Slash Pine [Steam preconditioned]	green, homogeneous, looking like a dry precipitate
9	Penrose, NSW	Radiata Pine	brown, high content of sawdust, wood, soil

*All samples collected in July 1990 except sample 8 which was collected in September 1989.

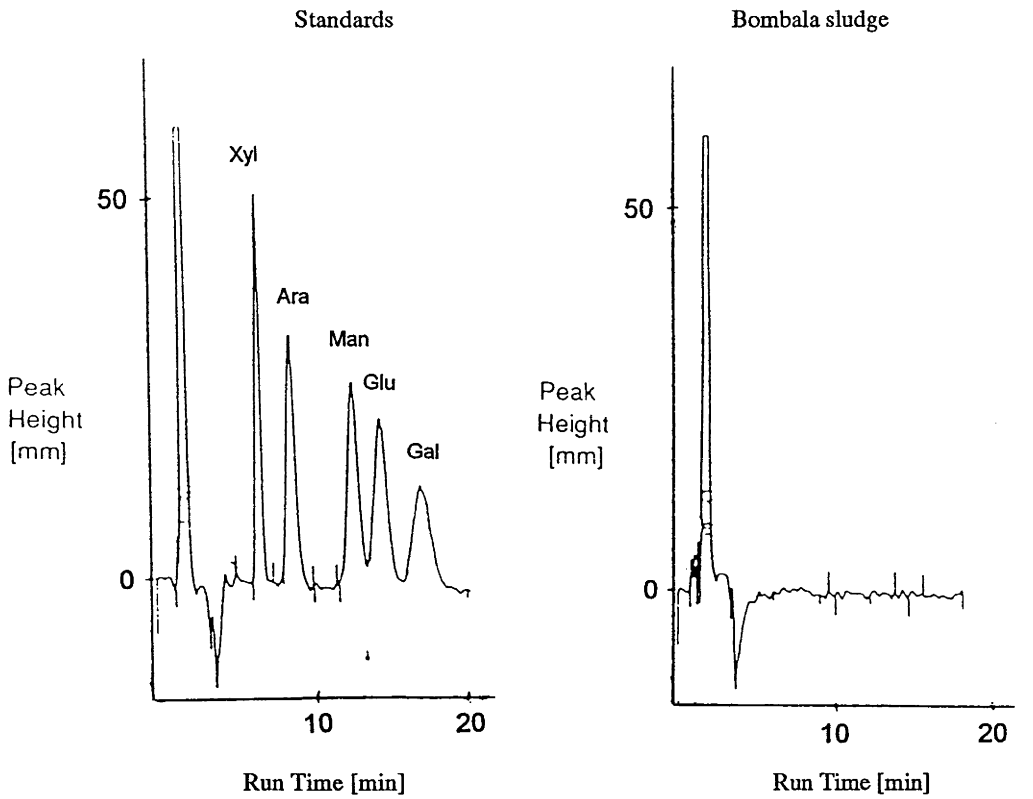
The moisture content of the sludges and the organic matter-lost on ignition are given in Table 9. Sludges 4 and 8 had high contents of physically bound water (WP), 13.7 and 14.0 %, respectively. This may be due to their very fibrous structure and high salt content which might provide a large surface area with a high adsorption capacity. Conversely sludges 1, 2, 6 and 7 have low moisture contents, below 5 %. These sludges contain a considerable amount of organic matter. With the exception of sludge 2, organic matter represents in excess of 10% by weight of the sludges.

Table 9. Moisture content (WP) and material lost on ignition (LI) of the sludges from Koppers treatment plants

Sludge	WP [w/w%]	LI [w/w%]
1	2.8	14.0
2	2.4	5.0
3	7.4	18.7
4	13.7	27.6
5	5.5	14.4
6	3.2	10.3
7	3.4	24.0
8	14.0	20.6
9	4.1	22.5

It was hypothesized that sugars, which in high concentration retard or destroy hydration reactions of cement (Wiles, 1989), might be leached from wood during treatment and form part of the sludge found in front sumps. However, somewhat surprisingly, chemical analysis using HPLC showed that all of the sludges were free of mono and disaccharides (Fig. 2). Possibly, Cr(VI) which is a strong oxidising agent reacts with the sugars resulting in degradation of the sugar carbon chains via bond cleavage (Mijs, 1986).

Fig. 2. HPLC traces for sugar solutions of D-xylose (xyl), D-arabinose (ara), D-mannose (man) D-glucose (glu) and D-galactose (gal) run as external standards and the leachate from Bombala sludge



The pH results are presented in Table 10. All of the sludges were mildly acidic. One can assume that Cr(VI) might have the greatest influence on pH. Sludges 6 and 2 have the lowest pH, of 2.59 and 3.39, respectively and also a higher Cr(VI) content (Table 13) than the other sludges. Sludge 1 appears to be almost neutral with a pH of 6.12. It is possible that the concentrations of soluble substances in this sludge, for example chromates, were reduced by washing before it was dried. During this procedure the acidity of the sample may have been reduced.

Table 10. pH of the sludges from Koppers treatment plants

Sludge	pH
1	6.12
2	3.39
3	4.24
4	4.34
5	3.56
6	2.59
7	4.44
8	4.77
9	3.40

The copper, chromium and arsenic contents of the sludges are presented in Table 11. As these elements are of environmental concern their concentrations in the sludges should be taken into account before formulating suitable solidification systems. Sludges 1, 2 and 7 had small amounts of Cu; i.e. 0.76, 0.87 and 0.65%, respectively. Sludges 4 and 8 were rich in Cu, 3.48 and 4.53 % respectively. Sludges 1, 2 and 7 had only 1.78, 1.91 and 1.76% of Cr respectively, while sludges 4 and 8 had 16.4 and 19.3 of Cr respectively. Of the 3 elements analysed arsenic had the highest concentration in the sludges. This accords with earlier observations on the chemical composition of synthetic CCA sludge. The As concentration in sludges 4, 5 and 6 was 26.19, 9.26 and 5.64 % respectively. If chromium salts are present in a significant concentration, they can impart a green colour to sludge and in general a green colour indicated that sludges had a high metal content. Thus sludges 4, 5 and 8 had the highest concentrations of metals and in contrast to other sludges (Table 8) had a green colour.

Table 11. Concentrations of copper, chromium and arsenic in the sludges from Koppers treatment plants

Sample	Cu [w/w%]	Cr [w/w%]	As [w/w%]
1	0.76	1.78	2.31
2	0.87	1.91	4.00
3	2.14	3.38	8.71
4	3.48	16.40	26.19
5	1.60	3.85	9.26
6	1.38	2.96	5.64
7	0.65	1.76	2.16
8	4.53	19.30	27.56
9	0.72	1.94	2.89

Inorganic material which was insoluble in perchloric and nitric acids formed a substantial part of the sludges. In sludges 1, 2, 3, 5 and 6 this inorganic component consisted of sand, gravel and the silicate and aluminate components of soil.

The concentrations of arsenic, chromium and copper in the sludges appeared to depend on the proportions of soil and sand and the amount of organic matter present, but the molar ratio of Cu : Cr : As depended more on the chemical composition of the CCA and on the treatment process used in the plant. The chemical composition of sludges is important when evaluating the suitability of solidification formulations for CCA sludge. The interactions of different elements with solidification reagents are likely to vary, hence their proportions in s/s systems could influence the results of leaching tests. The Cu : Cr : As molar ratio in the investigated sludges are given in Table 12. In general chromium and arsenic were in excess in those sludges, for example 4 and 8, which contained high levels of metals (Pizzi, 1982b).

Table 12. Cu : Cr : As molar ratio in the sludges from Koppers treatment plants

Sample	Mol.ratio		
	Cu	Cr	As
1	1	3.304	2.648
2	1	2.673	3.787
3	1	1.932	3.081
4	1	5.764	5.638
5	1	2.946	4.491
6	1	2.617	3.212
7	1	3.309	2.818
8	1	5.207	5.161
9	1	3.292	3.498

The concentration of water soluble Cr present in sludges is shown in Table 13. Soluble Cr determined in this work was in the form of CrO_4^{2-} or $Cr_2O_7^{2-}$. All chromates are very soluble in water and chromic acid has a large effect on pH. The highest concentration of Cr(VI) was found in sludges 5, 6 and 2; (1294, 1156 and 478 mg/kg, respectively). Pizzi (1981) has suggested that treated wood in sludges may also contain Cr(VI) bonded to lignin, but such complexes, if present, are likely to be insoluble in water and will not under normal circumstances be released into the aqueous environment (Pizzi, 1981). A yellow or light green colour of sludge reveals the presence of chromates.

Table 13. Concentrations of Cr(VI) in the sludges from Koppers treatment plants

Sample	Cr(VI) [mg/kg]
1	61
2	478
3	115
4	12
5	1294
6	1156
7	35
8	53
9	108

The concentrations of Fe, Ca, Mg, K and Na are shown in Table 14. Sludges 6 and 3 contain high amounts of iron, 17.59 and 9.02 %, respectively. Iron may in the cationic form act as a matrix disrupter or accelerator of cement hydration reactions (Wiles, 1987). Fe in the sludge may occur in the mineral form such as goethite, haematite or magnetite from soil or as a metal from corroded parts of treatment machinery or the plate on which sludges were dried. The presence of iron was evident during leaching of sludge as the electromagnetic stirrer was covered with iron particles. The concentrations of Ca, Mg, Na and K were very low. The amounts of Na in sludges 5, 6 and 8 were 0.70, 0.45 and 0.77 % respectively. Magnesium may act as a matrix disrupter and retarder of cement (Wiles, 1987) and might have a minor influence during the encapsulation of sludges 3 and 8.

Table 14. Concentrations of iron, alkali metals and alkaline earths in the sludges from Koppers treatment plants

Sample	Fe [w/w%]	Ca [w/w%]	Mg [w/w%]	Na [w/w%]	K [w/w%]
1	1.78	0.06	0.02	0.04	0.05
2	3.42	0.00	0.00	0.25	0.06
3	9.02	0.06	0.19	0.26	0.10
4	0.73	0.07	0.02	0.17	0.10
5	5.63	0.01	0.00	0.70	0.11
6	17.59	0.03	0.03	0.45	0.05
7	3.73	0.09	0.03	0.28	0.09
8	0.34	0.10	0.18	0.77	0.17
9	2.21	0.04	0.04	0.29	0.07

The concentrations of Cl and S in the sludges are shown in Table 15. Chlorides in small amounts, for example $CaCl_2 < 2\%$, have a positive effect on the hydration reactions of cements (Lea, 1970). Sulphur in the form of sulphate can have a detrimental effect on cement setting (Lea, 1970). Sludges 1 and 5 contained 0.18 and 0.16 % of Cl. Sludges 5

and 6 contained 0.45 and 0.43 % of S. These low concentrations of Cl and S present in the sludges are not likely to be detrimental for the setting of cement-sand mixes.

Table 15. Concentrations of chlorine and sulphur in the sludges from Koppers treatment plants

Sample	Cl [w/w%]	S [w/w%]
1	0.18	0.20
2	0.07	0.10
3	0.08	0.28
4	0.04	0.11
5	0.16	0.45
6	0.04	0.43
7	0.09	0.12
8	0.06	0.24
9	0.08	0.23

The concentrations of water soluble Cu, Cr and As in selected sludges were reduced by the addition of sawdust. The results are given in Appendix A and Fig. 3 and Fig. 4. The use of sawdust was very effective in reducing the concentration of all 3 soluble metals particularly in the Mogo sludge. The addition of 10% sawdust reduced the concentration of soluble Cr in the Mogo sludge from 1294 to 11 mg/kg (Fig. 3). The decrease in soluble As in the Mogo sludge after the addition of sawdust, from 904 to 139 mg/kg was also significant (Fig. 3). The addition of sawdust was not so effective in the case of Penrose sludge (Fig. 4). Only soluble Cr was reduced from 108 to 15 mg/kg (Fig. 4). The reduction of Cr(VI) to Cr(III) in the presence of high concentration of Cu and As results in the formation of insoluble copper arsenates, chromium arsenates and copper chromates. However, at low concentrations Cr(VI) might be reduced by sawdust to chromium hydroxide or be bound to wood components. In the latter case chromium does not form insoluble compounds with Cu and As (Pizzi, 1982a) and this may explain why the addition of sawdust to the Penrose sludge was relatively ineffective in reducing the concentrations of Cu and As.

Fig. 3. Concentration of water-soluble Cu, Cr and As in the Mogo sludge after the addition of 10% and 20% of sawdust

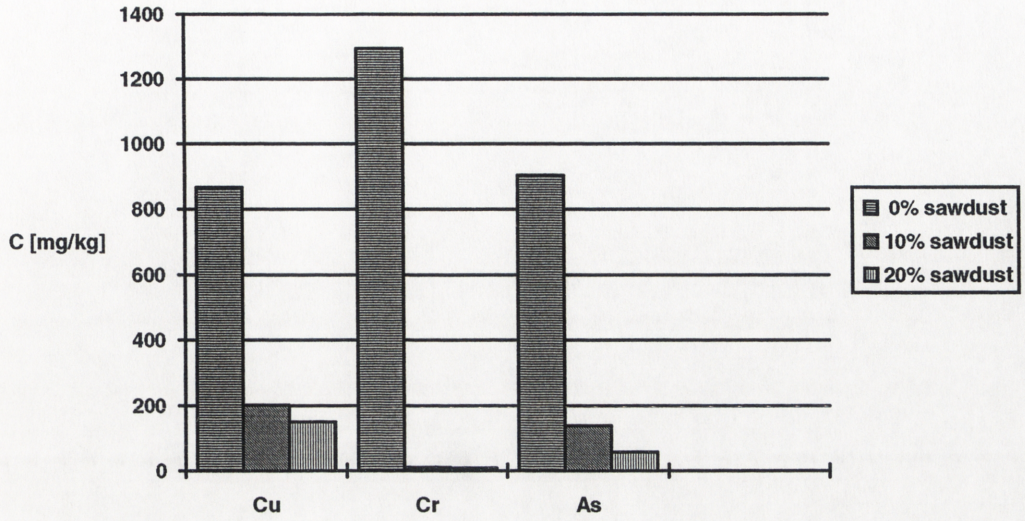
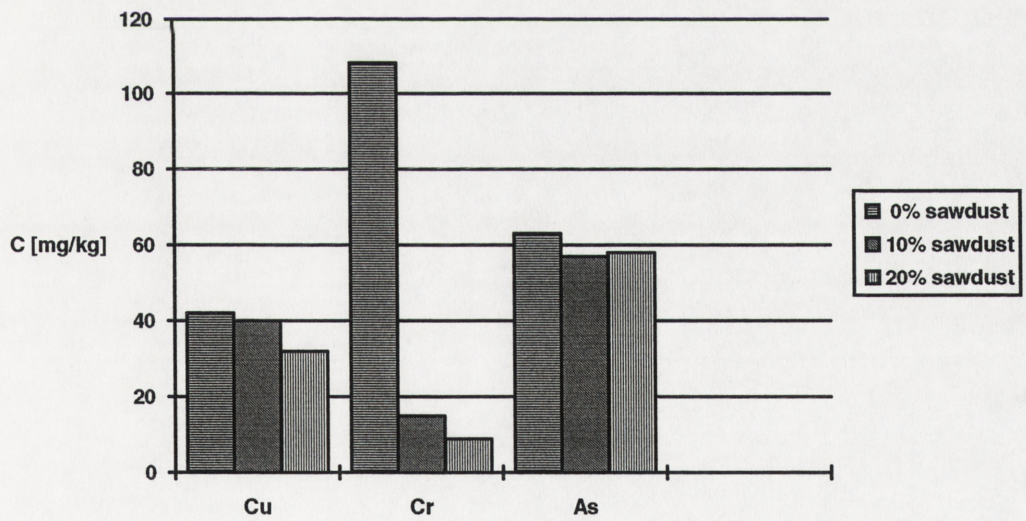


Fig. 4. Concentration of water-soluble Cu, Cr and As in the Penrose sludge after the addition of 10% and 20% of sawdust



3.3. Summary

Analyses of sludges from eight commercial treatment plants revealed that their character varied from plant to plant. Most of the sludges contained significant amounts of

extraneous materials such as soil and wood. The Narangba sludges which were not reduced by the components of soil or a significant amount of sawdust had higher concentrations of copper, chromium and arsenic than the other sludges. Treatment conditions and perhaps the design of some plants which allows extraneous materials to enter the treatment process and subsequently to become components of sludge appeared to be important factors affecting the composition of sludges. The synthetic sludge differed significantly from the commercial plant sludges since it was not affected by the specific treatment conditions and did not contain extraneous materials such as soil, wood and iron.

The concentration of soluble metal compounds may be an important factor determining the environmental stability of hazardous wastes treated using s/s processes (Conner, 1990). In order to clarify this suggestion, Penrose and Mogo sludges were pretreated using sawdust as a reducing agent prior to cement-based stabilisation/solidification process which was investigated in the following work.

Chapter 4. Stabilisation/solidification of synthetic or relatively pure CCA sludges

The components of sludge may affect its encapsulation. Therefore synthetic sludge and also pure copper, chromium and arsenic compounds were used to investigate the effect of CCA components on cement-sand matrices. The leachability of copper, chromium and arsenic from s/s samples and their unconfined compressive strength and morphology were analysed.

4.1. Materials and methods

4.1.1. CCA sludge from CSR-Permalog Narangba plant

The sludge from CSR-Permalog Narangba plant contained little extraneous material; the concentration of Cu, Cr and As was similar to the synthetic laboratory prepared sludge (Table 11). Therefore, this sludge was used to study the leaching of Cu, Cr and As from cement-stabilised samples. Sludge was air dried on a steel plate for 2 weeks, oven dried at 105 °C and its moisture content determined.

4.1.2. Preparation of solidified samples

Two kinds of collapsible moulds were prepared: cylindrical moulds for leaching tests and cubic moulds for compressive strength tests. The cylindrical mould consisted of 3 parts; a column composed of PVC-tube, 105 mm in diameter cut along its axis with the two identical halves screwed to a teflon base 10 mm thick. The cubic moulds were made of 25 mm thick PVC-board. The walls of the cube were assembled with 4 stainless steel screws. The base of the mould was 25 mm thick and was attached to the walls by 2 screws.

The Portland cement used in the experiments was Kandos cement. Its chemical composition is given in Table 16.

Table 16. Composition of Kandos Portland cement

CaO [w/w%]	Al_2O_3 [w/w%]	Fe_2O_3 [w/w%]	SiO_2 [w/w%]	MgO [w/w%]	SO_3 [w/w%]
64.0	5.0	3.5	22.0	1.5	2.5

Since there are 4 components of solidified products (sludge, cement, sand and water) which influence the quality of the solidified product, experiments were conducted to evaluate the effect of variations in cement-sand formulation and sludge quantity on the leaching of Cu, Cr, As from solidified blocks. The effect of variation in cement-sand and sludge quantities on the compressive strength of solidified blocks was also analysed.

To evaluate the effect of Cr(VI) on leaching of chromium from solidified product, CrO_3 was also added to some samples. The constituents are expressed in weight proportions. For samples containing air-dry sludge from Narangba (NA), the amounts of sludge added were recalculated to take into account the water content of the sludge, i.e. the amounts of sludge added were slightly higher.

Approximately 700 g of dry sand, cement and sludge were weighed into a 2000 mL beaker and the mix was homogenised with a laboratory spoon. Water was then added and the sample was mixed for 4 minutes. The mixture was poured into a cubic and a cylindrical mould and was then pressed using a plunger to fill the moulds thoroughly. Both samples were generally taken out of the moulds after 24h. They were then placed in a polyethylene sack and cured for 28 days at room temperature. After 28 days the cylindrical samples were crushed and separated into 4 fractions (0.0-0.1 mm, 1.0-2.0 mm, 3.9-5.2 mm and 5.2-9.5 mm) using sieves with the following mesh sizes, 1.0 mm, 2.0 mm, 3.9 mm, 5.2 mm and 9.5 mm.

4.1.3. Preparation of Cr(III), Cr(VI), Cu(II), As (III) and As(V)-bearing cement-sand mixes

In order to interpret the leaching patterns of cement-stabilised CCA wastes, samples containing pure Cu, Cr and As were prepared. Chromium in the form of Cr_2O_3 (Cr III) and CrO_3 (CrVI) As in the form of As_2O_3 (As III) and As_2O_5 (As V) and Cu in the form of $CuSO_4.5H_2O$ (Cu II) were added to a cement-sand mix and the samples were cured in an environment cabinet at 20 °C. The samples for TCLP tests were cured for 28 days and the cubes for unconfined compressive strength measurement were cast and were also cured for 26 days (as above). After this the samples for unconfined compressive strength measurement were put in saturated $Ca(OH)_2$ solutions for 2 days before testing. (ASTM, 1987) The samples for SEM observations were cured at 20 °C for 7 days.

4.1.4. Leaching tests of solidified wastes

After 28 days of curing, samples were tested for leaching of copper, chromium and arsenic using a modified TCLP as follows:

12.5 g of a crushed solidified sample (particles smaller than 9.5 mm) was weighed and placed in a 300 mL-beaker and 250 mL of dilute acetic acid at pH 2.8 was added. The mixture of solidified sample and acid was agitated for 18h using a magnetic stirrer and it was then filtered into a 250 mL-volumetric flask using filter paper No. 42. The quantities of metals (Cr, Cu, As) dissolved in the acetic acid after the extraction period were determined using AAS (as described in Section 3.1.2.5).

4.1.5. Unconfined compressive strength measurement

Measurement of unconfined compressive strength of s/s stabilised waste was carried out using a Shimadzu testing machine REH-30 (ASTM, 1987). The tests were performed using the 50 mm cubes.

4.2. Results

4.2.1. Leaching results

Leaching of metals from synthetic sludge incorporated in cement-sand occurred during the TCLP test (Table 17). These samples were reduced to a particle size of 0-9.5 mm prior to the leaching test. The leachability of Cu was very low for all of the samples and did not exceed 0.1 mg/L. Similarly the concentrations of Cr and As in the leachates were relatively small in comparison to the metal content of the cement-sand forms. For example, less than 0.1 % of As in sample 5 (Table 17) was present in the leachate.

Table 17. Leachability of Cu, Cr and As from cement-sand samples containing chemically pure CCA sludge

Sample	Cement:Sand: H_2O: sludge [weight parts]	Metal addition [mg/kg]			Metal concentration in the leachate [mg/L]		
		Cu	Cr	As	Cu	Cr	As
1	1:2:0.4:0.02	430	940	1820	0.05	0.13	0.2
2	1:2:0.4:0.04	860	1870	3610	0.06	0.23	0.1
3	1:2:0.4:0.06	1290	2790	5380	0.04	0.21	0.4
4	1:2:0.4:0.09	1910	4140	8010	0.04	0.22	0.2
5	1:2:0.4:0.12	2530	5480	10590	0.04	0.14	0.5

The concentrations of Cu, Cr and As in the leachates are given for four fractions of solidified particles; fraction a=0.0-0.1, b=0.1-0.2, c=3.9-5.2 and d=5.2-9.5 mm (Table 18). The leaching of metals from s/s synthetic sludge did not depend on the size of solidified particles. When the cement-sand matrices containing synthetic sludge were reduced to particles less than 0.1 mm in size, the leachability of Cu, Cr and As did not increase in comparison to bigger particles. Also the amount of water used to prepare sand-cement matrices did not affect metal leachability (Tables 17 and 18). The concentration of Cu in all of the leachates was not higher than 0.1 mg/L. Generally, the synthetic CCA sludge in all of the cement-sand matrices (Tables 17 and 18) was safely

stabilised and one can hardly discern any trend in the leaching results with regard to the effect of adding sludge to the matrices. Due to the larger surface area one might expect, as was observed by Butler (1990), a higher metal concentration after leaching of finer particles, but in these experiments this was not the case. For example the concentration of As in the leachates of samples 1 and 3 for particle sizes less than 0.1 mm was 0.3 and 0.1 mg/L respectively, whereas the As concentration in the leachates from samples of a particle size 5.2-9.5 mm was also 0.1 and 0.3 mg/L.

Table 18. Leachability of Cu, Cr and As from cement-sand samples containing synthetic CCA sludge: Effect of particles sizes

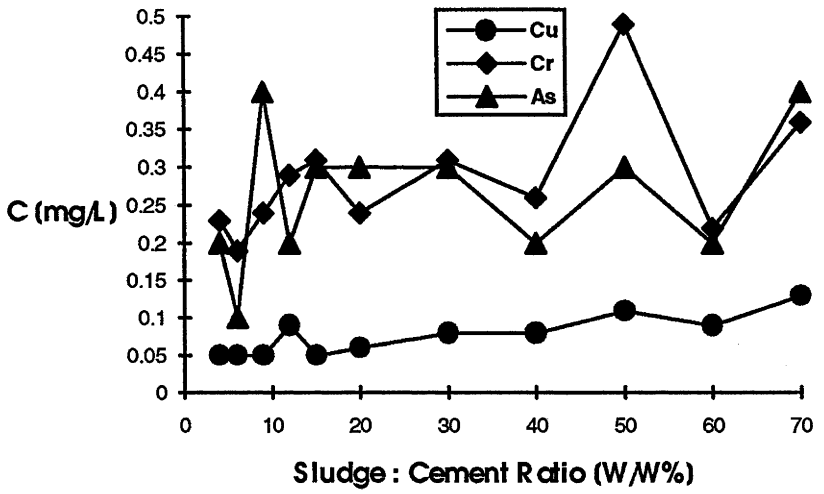
Sample	Cement:Sand: H_2O [weight parts]	Particle size [mm]	Metal addition [mg/kg]			Metal concentration of the leachate [mg/L]		
			Cu	Cr	As	Cu	Cr	As
1	1:2:0.5:0.02	0.0-0.1	420	910	1760	0.06	0.25	0.3
1	1:2:0.5:0.02	0.1-0.2	420	910	1760	0.06	0.25	0.0
1	1:2:0.5:0.02	3.9-5.2	420	910	1760	0.04	0.21	0.2
1	1:2:0.5:0.02	5.2-9.5	420	910	1760	0.10	0.19	0.1
2	1:2:0.5:0.04	0.0-0.1	840	1820	3510	0.06	0.12	0.1
2	1:2:0.5:0.04	0.1-0.2	840	1820	3510	0.05	0.20	0.2
2	1:2:0.5:0.04	3.9-5.2	840	1820	3510	0.05	0.20	0.2
2	1:2:0.5:0.04	5.2-9.5	840	1820	3510	0.05	0.23	0.1
3	1:2:0.5:0.06	0.0-0.1	1250	2710	5230	0.04	0.21	0.1
3	1:2:0.5:0.06	0.1-0.2	1250	2710	5230	0.05	0.18	0.2
3	1:2:0.5:0.06	3.9-5.2	1250	2710	5230	0.04	0.16	0.1
3	1:2:0.5:0.06	5.2-9.5	1250	2710	5230	0.10	0.16	0.3
4	1:2:0.5:0.09	0.0-0.1	1860	4030	7780	0.07	0.23	0.2
4	1:2:0.5:0.09	0.1-0.2	1860	4030	7780	0.05	0.17	0.3
4	1:2:0.5:0.09	3.9-5.2	1860	4030	7780	0.04	0.18	0.2
4	1:2:0.5:0.09	5.2-9.5	1860	4030	7780	0.10	0.16	0.2
5	1:2:0.5:0.12	0.0-0.1	2460	5330	10290	0.05	0.25	0.1
5	1:2:0.5:0.12	0.1-0.2	2460	5330	10290	0.05	0.17	0.3
5	1:2:0.5:0.12	3.9-5.2	2460	5330	10290	0.05	0.18	0.0
5	1:2:0.5:0.12	5.2-9.5	2460	5330	10290	0.08	0.21	0.2

The leaching results for encapsulated sludge from the Narangba treatment plant are shown in Table 19 and Fig. 5. As for cement-stabilised synthetic sludge, the stability of these samples was high. The metal concentration in all of the leachates was negligible. For example, although 41200 mg/kg As was added to sample 11, the As concentration of the leachate was 0.4 mg/L. Thus only 0.2% of the As added to the cement-sand matrix was present in the leachate. Also the Cu and Cr concentrations of all leachates were very small, less than 0.2 and 0.4 mg/L respectively. The metal leachability did not change when additional sludge was added to the samples. Thus the leachability of Cu, Cr and As from samples 1 and 10 was approximately the same, even though the amount of metal added to sample 10 was 10 times greater than to sample 1.

Table 19. Leachability of Cu, Cr and As from cement-sand samples containing Narangba sludge

Sample	Cement:Sand: H_2O:Sludge [weight parts]	Metal addition to the concrete [mg/kg]			Metal concentration in the leachate [mg/L]		
		Cu	Cr	As	Cu	Cr	As
1	1:2:0.5:0.04	390	1850	2960	0.05	0.23	0.2
2	1:2:0.5:0.06	590	2760	4410	0.05	0.19	0.1
3	1:2:0.5:0.09	870	4110	6570	0.05	0.24	0.4
4	1:2:0.5:0.12	1150	5440	8680	0.09	0.29	0.2
5	1:2:0.5:0.15	1430	6740	10760	0.05	0.31	0.3
6	1:2:0.5:0.2	1880	8860	14160	0.06	0.24	0.3
7	1:2:0.5:0.3	2750	12950	20680	0.08	0.31	0.3
8	1:2:0.6:0.4	3480	16400	26190	0.08	0.26	0.2
9	1:2:0.7:0.5	4140	19520	31180	0.11	0.49	0.3
10	1:2:0.7:0.6	4860	22880	36500	0.09	0.22	0.2
11	1:2:0.75:0.7	5470	25800	41200	0.13	0.36	0.4

Fig. 5. Cu, Cr and As concentration in the leachates of samples with addition of Narangba sludge (x sludge, 100 cement, 200 sand)



Since the Narangba sludge contained only trace amounts of Cr(VI) (Table 20), CrO_3 was added to some of the formulations. The results in Table 20 indicate that the cement matrix was not effective in retaining Cr(VI). Sample 1 which contained 1160 mg of Cr(VI) to 1 kg of sand-cement did not pass the leaching test since the Cr concentration of the leachate was 57 mg/L, i.e. in excess of 52 mg/L, the permissible limit. Similarly other samples which contained higher amounts of Cr(VI) did not pass the standard leaching test for Cr. The addition of CrO_3 significantly increased the Cr concentration of all leachates. Assuming only a small amount of chromium in the leachates originated from sludge, approximately 88% of CrO_3 was leached from sample 1. Cement-sand matrices failed to contain Cr(VI) within their structure. Also the Narangba sludge probably did not reduce CrO_3 solubility. On the other hand the addition of CrO_3 did not increase the amount of arsenic released from sludge.

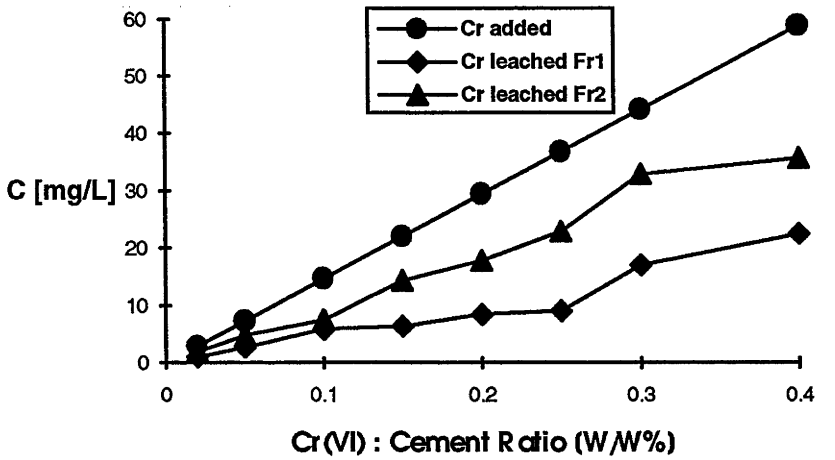
Table 20. Leachability of Cu, Cr and As from cement-sand samples containing Narangba sludge and CrO_3

Sample	Cement:Sand: H_2O:sludge [weight parts]	Cr(VI) addition by CrO_3 [mg/kg]	Metal addition [mg/kg]			Metal concentration in the leachate [mg/L]		
			Cu	Cr	As	Cu	Cr	As
1	1:2:0.5:0.6	1160	5090	24000	38330	0.10	51.2	0.7
2	1:2:0.5:0.6	2320	5090	24000	38330	0.12	91.0	0.4
3	1:2:0.5:0.6	4640	5090	24000	38330	0.12	135.8	1.3
4	1:2:0.5:0.6	6960	5090	24000	38330	0.13	265.4	0.8

The leaching results of samples bearing pure Cr, Cu and As compounds are given in Appendices B, C, D, E and F and Figures 6 - 10.

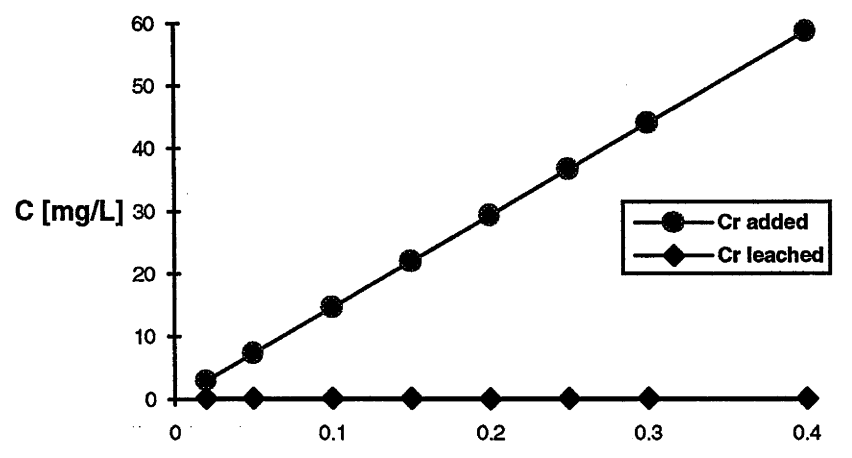
The leaching results for samples containing Cr(VI) (Appendix B) indicated that the leachability of Cr increased with the addition of Cr(VI). The concentration of chromium in leachates was also dependent on particle size (Fig. 6). Thus particles smaller than 0.3 mm (Fraction 2) released more Cr than particles smaller than 6 mm (Fraction 1). Approximately 30% of Cr from fraction 1 and 60% of Cr from fraction 2 were released during leaching. Cr(VI) did not appear to be immobilised by the cement-sand matrix. Thus, the concentration of Cr_{added} in Fig. 6 indicates that virtually all Cr added to the cement-sand matrices would be extracted by acetic acid.

Fig. 6. Cr concentration in the leachate of samples with the addition of CrO_3 (xCr(VI), 100 cement, 200 sand); Fr1 - particles smaller than 6 mm, Fr2 - particles smaller than 0.3 mm



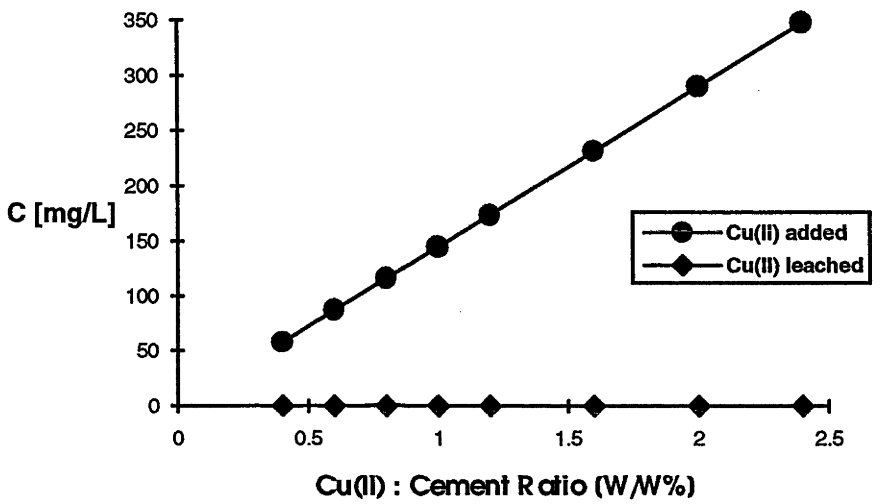
The leachability of Cr(III) from cement-sand matrices, in contrast to Cr(VI), was very limited (Appendix C and Fig. 7). For example only 0.3 % of Cr added to sample 8 was leached during the TCLP test. The concentration of Cr released did not increase when additional of Cr_2O_3 was added to samples.

Fig. 7. Cr concentration in the leachate of samples with the addition of Cr_2O_3 (x Cr(III), 100 cement, 200 sand)



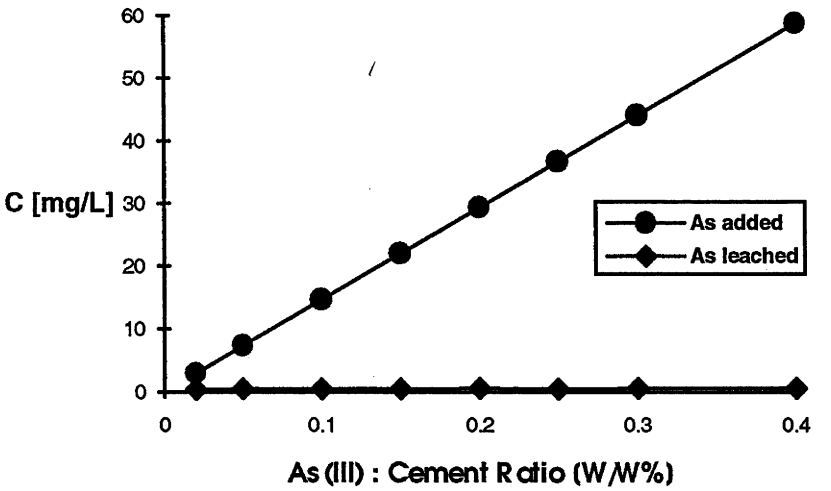
The leaching results for samples containing Cu(II) in the range 1200-7200 mg/kg indicate that Cu was safely incorporated within a cement-sand matrix (Appendix D and Fig. 8). The concentration of Cu in the leachate from sample 8 was 0.1 mg/kg, thus only 0.03 % of the Cu added to the matrix was extracted by the leaching solution.

Fig. 8. Cu concentration in the leachate of samples with the addition of $CuSO_4.5H_2O$ (x Cu(II), 100 cement, 200 sand)



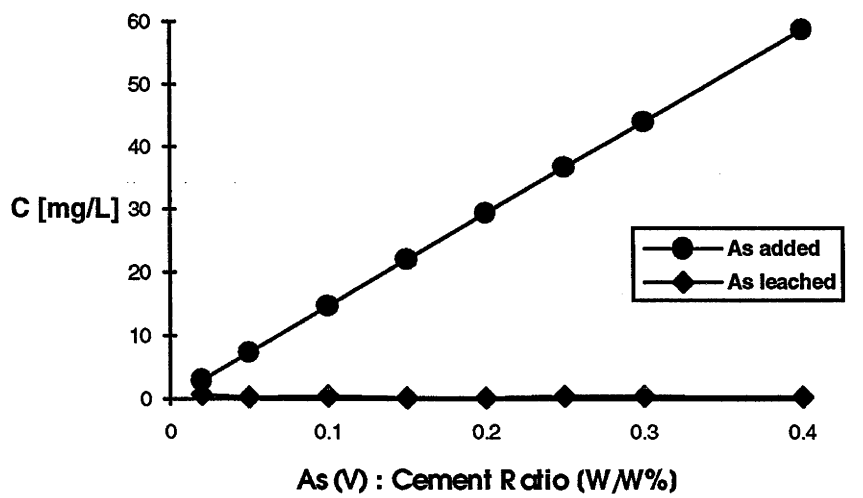
Leaching of arsenic from s/s samples containing pure arsenic compound was also low. Thus the environmental acceptability of samples containing As(III) in the form of As_2O_3 at concentrations of 60-1050 mg/kg was within the criteria for disposal by landfill. The As concentration of all the leachates was less than 0.6 mg/L (Appendix E and Fig. 9).

Fig. 9. As concentration in the leachate of samples with the addition of As_2O_3 (x As (III), 100 cement, 200 sand)



In accord with results for As_2O_3, As_2O_5 in the range 60-1050 mg/kg was also safely contained within the sand-cement matrices (Appendix F and Fig. 10). As_2O_5 is normally very soluble, but during s/s it probably reacts with the products of cement hydration forming insoluble calcium arsenate and is therefore resistant to acid leaching.

Fig. 10. As concentration in the leachate of samples with the addition of As_2O_5 (x As (V), 100 cement, 200 sand)



All solidified samples containing only synthetic or Narangba sludge without the addition of Cr(VI) showed small losses of metals after leaching with dilute acetic acid. The samples without the added Cr(VI) passed the environmental requirements for Cu, Cr and As (Victoria EPA, 1986). The concentrations of Cu, Cr and As in all of the solutions were very low, (under 0.5 mg/L). Thus synthetic sludge and the Narangba sludge were stabilised by cement and the leachability of Cu, Cr and As from s/s sludge was insignificant. Copper arsenates and chromium arsenates which are the principle components of sludge (McMahon *et al.*, 1942), are probably stable in the alkaline environment of cement solutions. The Cr concentration of leachates used to extract s/s samples clearly depends on the Cr(VI) content of the sludge. Cr(III), Cu(II), As(III), and As(V) added to the cement-sand matrices in the form of pure compounds (Appendices B-F) were not extracted by acetic acid. Thus at low concentrations these metal compounds can be stabilised by cement-sand matrices.

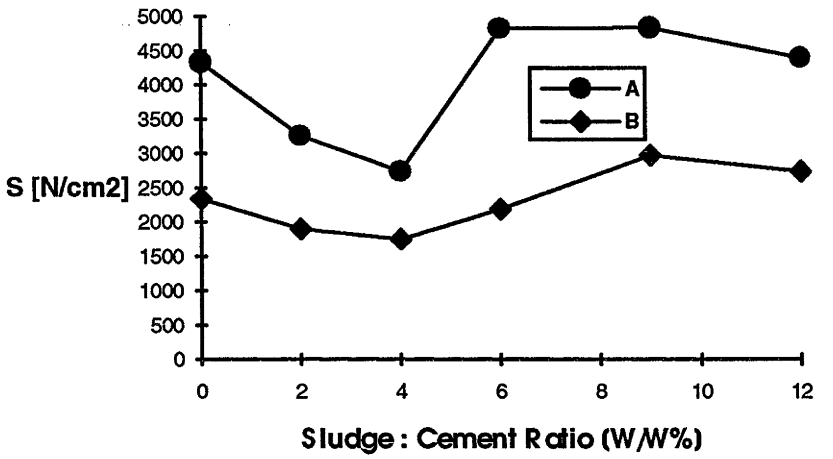
Since the quantity of Cr(VI) in the sludge appears to be one of the most significant factors influencing the release of chromium into acid leachates, stabilisation/solidification treatments should focus on methods of reducing Cr(VI) in CCA sludge so that it can then be safely encapsulated into cement-sand.

4.2.2. Compressive strength results

The results of compressive strength tests on cement-sand samples containing synthetic sludge are shown in Appendices G and H and Fig. 11. These results indicate that the water content of samples significantly affected the compressive strength of test blocks. Thus the compressive strength of blocks with the addition of 0.4 part of water to 1 part of cement and 2 parts of sand was considerably higher than for samples with the same solids content but containing 0.5 part of water (Fig. 11). For example, the compressive strength of samples prepared from 1 part of cement, 2 parts of sand, 0.12 parts of the sludge and 0.5 parts of water was 2740 N/cm^2, while the samples prepared with 0.4

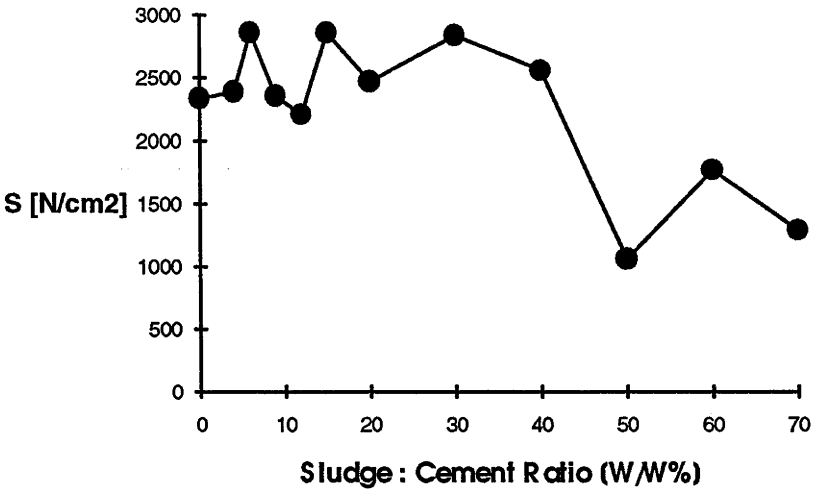
parts of water had a compressive strength 4390 N/cm^2. Thus for low levels of sludge in solidified samples, 40 weight parts of H_2O added to 100 weight parts of cement and 200 weight parts of sand seemed to be optimal (Fig. 11).

Fig. 11. Compressive strength of the cement-sand samples with addition of 0.4(A) and 0.5(B) parts of water per 1 part of cement (x synthetic sludge, 100 cement, 200 sand)



The addition of small amounts of CCA sludge to samples did not reduce the compressive strength of blocks. For example, the addition of 40 weight parts of Narangba sludge into samples (Appendix I and Fig. 12) did not reduce compressive strength, but at higher sludge concentrations strength was reduced. However, this might be caused by an inappropriate water content in these samples, since dry sludge consumes a significant amount of water and therefore the quantity of water available to participate in the hydration of cement might be inadequate.

Fig. 12. Compressive strength of the cement-sand samples containing Narangba sludge (x sludge, 100 cement, 200 sand, 50H2O)



The compressive strength for the samples containing pure Cu, Cr and As compounds is given in Table 21. As(V) and Cu(II) greatly reduced the compressive strength of samples. The addition of 2930 mg of metals in the form of As_2O_5 and $CuSO_4.5H_2O$ respectively to 1 kg of cement-sand had a much greater effect on compressive strength than the addition of higher levels of metals in the form of Narangba sludge (Appendix I). Thus samples with the addition of Narangba sludge contained almost the same amount of As (sample 2, Appendix I) as samples containing arsenic in the form of As_2O_5 but their compressive strength was 40 times higher. The effect of adding As(III), Cr(III) and Cr(VI) on compressive strength was less significant. The samples with the addition of As_2O_3, Cr_2O_3, and CrO_3 had compressive strengths of 990, 1720, and 950 N/cm^2 respectively.

Table 21. Compressive strength of cement-sand samples containing 100 parts of cement, 200 parts of sand, 40 parts of water and 2 parts of metal

Sample	Cement:Sand: H_2O: metal [weight parts]	Metal	Compound	Compressive Strength [N/cm^2]
1	1:2:0.4:0.02	As(III)	As_2O_3	990
2	1:2:0.4:0.02	As(V)	As_2O_5	60
3	1:2:0.4:0.02	Cr(III)	Cr_2O_3	1720
4	1:2:0.4:0.02	Cr(VI)	CrO_3	950
5	1:2:0.4:0.02	Cu(II)	$CuSO_4.5H_2O$	140

4.2.3. SEM results

SEM images of cement with and without the addition of metals are presented in Micrographs 1-12. The micrographs of samples were taken after 7 days of curing to identify the effect of adding the metals on the structure of the hydrated cement. Micrographs 1-2 are of pure Portland cement, micrographs 3-6 show chromium bearing cement, micrographs 7-8 show copper bearing cement and micrographs 9-12 show arsenic bearing cement.

SEM photomicrographs (3-4) show that the structure of hydrated cement after the addition of Cr(III) does not differ substantially from the hydrated cement controls (Micrographs 1-2). The microstructure of these cements was dominated by ettringite crystals (Mindess and Young, 1981). Ettringite is calcium sulfoaluminate hydrate whose formula is $3CaO.Al_2O_3.3CaSO_4.31H_2O$. These crystals are formed at an early stage of the hydration of cement by reaction of tricalcium aluminate, $3CaO.Al_2O_3$, with gypsum, $CaSO_4$. Although the Cr(III)-bearing cement contained more ettringite crystals, the shape and size of crystals in both samples were similar. It appears that Cr(III) did not have a significant effect on the structure of cement. This finding correlates with

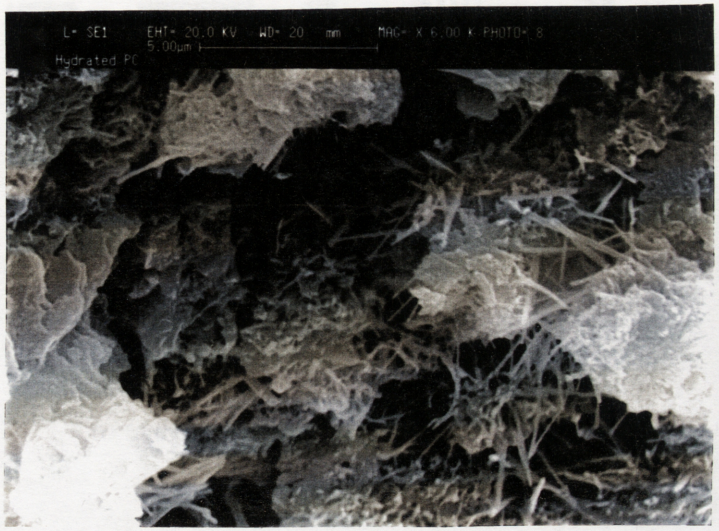
compressive strength measurements since Cr(III) did not reduce the strength of cement-sand matrices as much as the addition of the other metals.

Besides ettringite clusters the microstructure of Cr(VI)-bearing cement was characterised by plate shape crystals of monosulphoaluminate, $4CaO.Al_2O_3.SO_3.12H_2O$ (Micrographs 3-4). It was suggested (Mindess and Young, 1981) that the crystal needles of ettringite might convert to the platy morphology of monosulphoaluminate,

The addition of Cu(II) in the form of $CuSO_4.5H_2O$ significantly affected the structure of cement. The microstructure of this cement was characterised by very large ettringite crystals (Micrographs 7-8). The development of these crystals was probably enhanced by the addition of sulphate which may provide ions for crystal growth. It has been found previously that Cu(II) in the form of $Cu(OH)_2$ has a considerable influence on the crystal growth of ettringite and the structure of cement (Tashiro *et al.,* 1979). The present work supports these findings. SEM micrographs reveal little evidence of hydration of calcium silicates after 7 days of curing and this may be due to the effect that soluble Cu(II) has on retarding the hydration (Mindess and Young, 1981). Also the lower compressive strength of Cu(II)-bearing sand-cement matrices indicates that the addition of Cu(II) retarded setting and hardening.

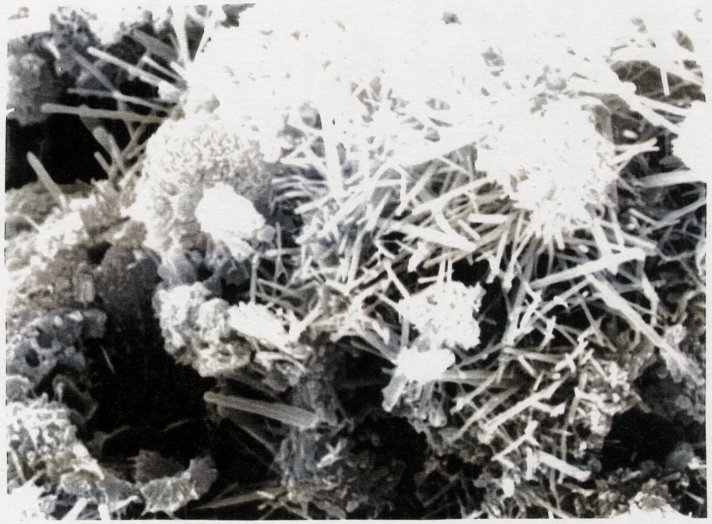
Surprisingly, As_2O_3 and As_2O_5 had different effects on cement microstructure. While As(III)-bearing cement possessed needle crystals (Micrographs 9-10), the matrices of As(V)-bearing cement consisted of crystals which were scattered and badly defined structurally (Micrographs 11-12). As(V)-bearing sand-cement matrices were also weak. Thus it appears that As_2O_5 retards setting and hardening. XRD measurements of As(V)-bearing sand-cement matrices after 28 days of curing did not detect portlantide, $Ca(OH)_2$, which is a product of the hydration of cement (Aldridge, 1992). On the other hand As(III)-bearing cement-sand matrices were found to contain portlantide.

While $CuSO_4.5H_2O$, CrO_3 and As_2O_5, as SEM micrographs and compressive strength measurements indicate, had detrimental effects on cement-sand matrices, the addition of sludge did not significantly decrease strength. Thus, unlike the water soluble components of CCA treatment solutions, insoluble copper arsenates and chromium arsenates had benign effects on the structural properties of cement-sand matrices.



Micrograph 1. Portland cement after 7 days of hydration

Micrograph 2. Portland cement after 7 days of hydration

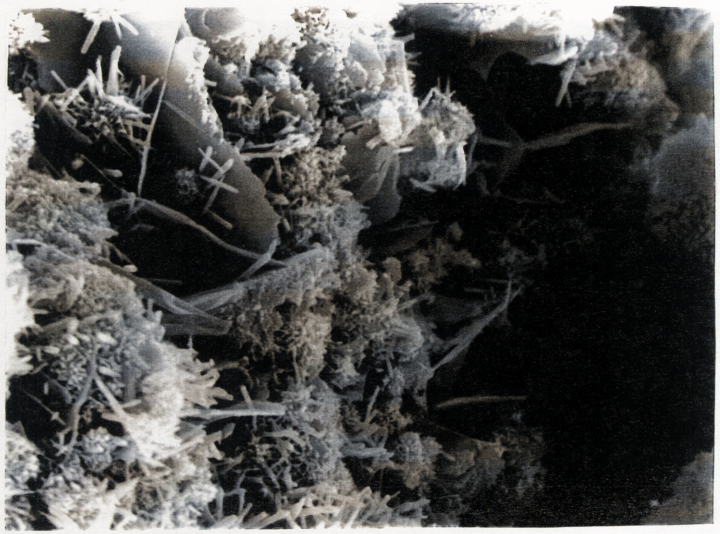


Micrograph 3. Portland cement with 1% additional Cr(III) (Cr_2O_3) after 7 days of hydration

Micrograph 4. Portland cement with 1% additional Cr(III) (Cr_2O_3) after 7 days of hydration

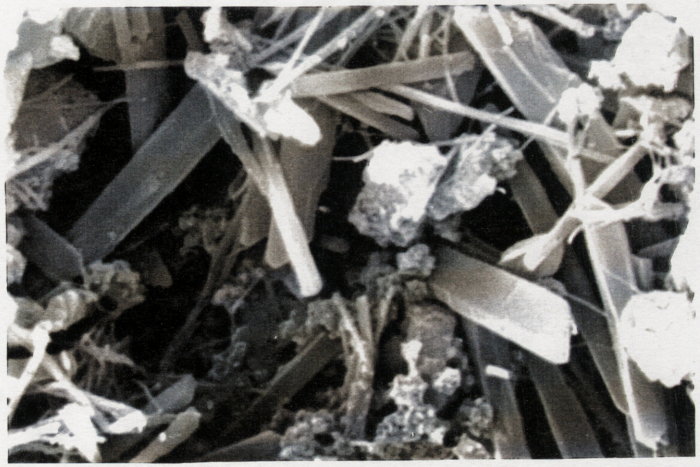
5.0 μm

Micrograph 5. Portland cement with 1% additional Cr(VI) (CrO_3) after 7 days of hydration



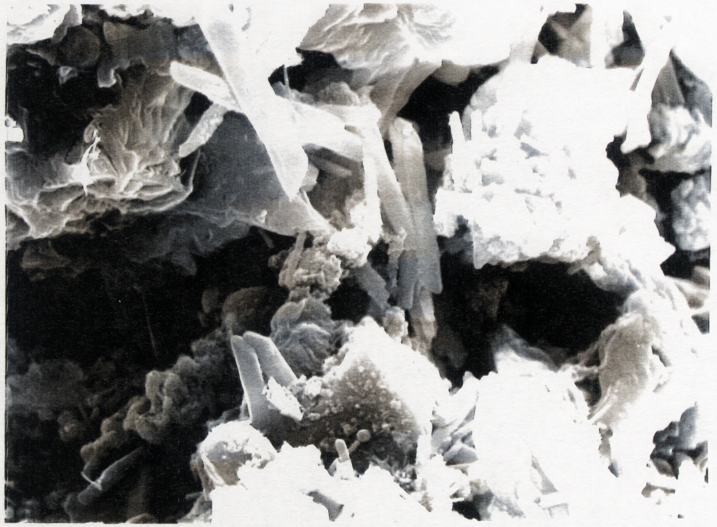
5.0 μm

Micrograph 6. Portland cement with 1% additional Cr(VI) (CrO_3) after 7 days of hydration



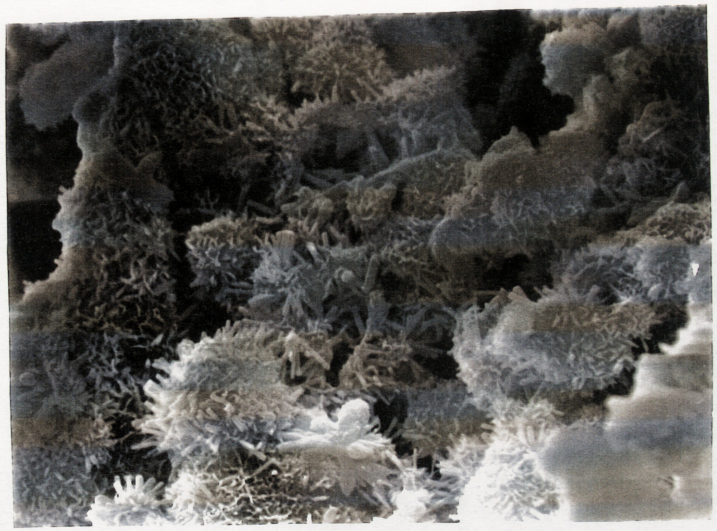
2.0 μm

Micrograph 7. Portland cement with 1% additional Cu(II) ($CuSO_4.5H_2O$) after 7 days of hydration



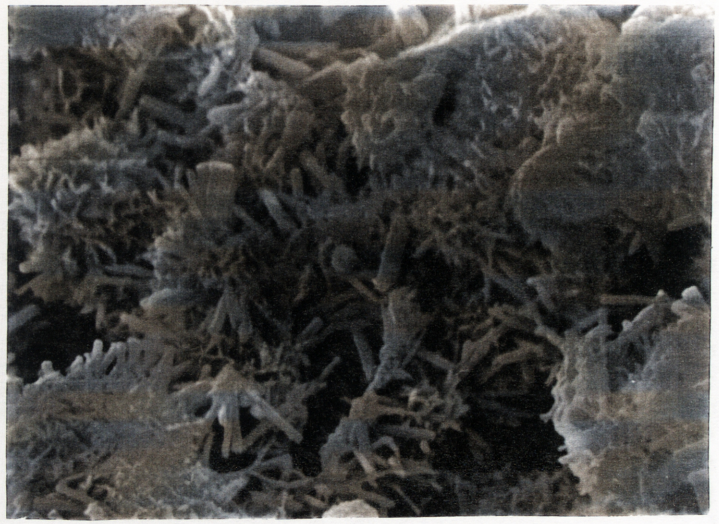
5.0 μm

Micrograph 8. Portland cement with 1% additional Cu(II) ($CuSO_4.5H_2O$) after 7 days of hydration



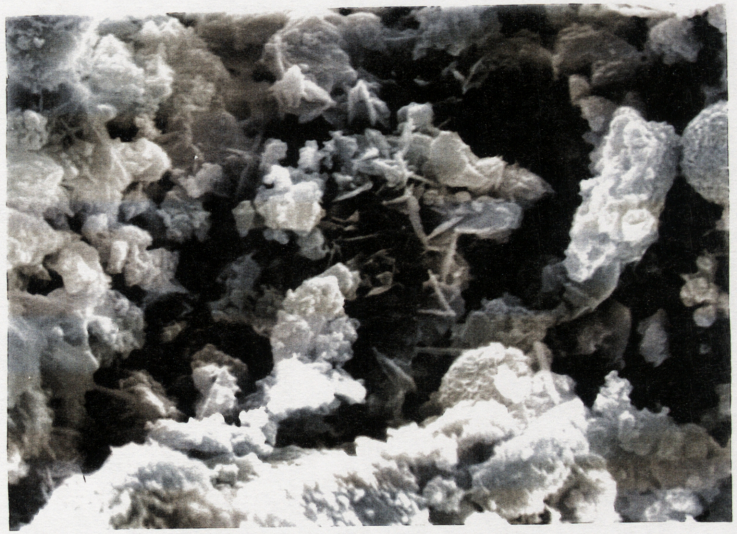
5.0 μm

Micrograph 9. Portland cement with 1% additional As(III) (As_2O_3) after 7 days of hydration



2.0 μm

Micrograph 10. Portland cement with 1% additional As(III) (As_2O_3) after 7 days of hydration



5.0 μm

Micrograph 11. Portland cement with 1% additional As(V) (As_2O_5) after 7 days of hydration

5.0 μm

Micrograph 12. Portland cement with 1% additional As(V) (As_2O_5) after 7 days of hydration

Chapter 5. Stabilisation/solidification of the sludges from commercial treatment plants

The leachability of copper, chromium and arsenic from cement-sand matrices containing sludges from commercial treatment plants was examined. Sludges whose cement-sand matrices showed higher leachability were pretreated by hardwood (*E. fastigata*) sawdust prior to the s/s process.

5.1. Materials and methods

Sludges from both softwood (Penrose, Bombala and Hume) and hardwood (Mogo) treatment plants were selected for stabilisation treatments. Untreated sludges and sludges treated with sawdust were added to cement-sand mixes. The samples were then placed in plastic bags and cured in a controlled environment cabinet at 20 °C for 28 days. During the last 7 days the bags were left open to allow the samples to release water that was not consumed by the hydration of cement. Since some of the samples still contained adsorbed water, the samples were further air dried for 1 day. The samples were then leached using the TCLP procedure and the pH of the leachate determined. The concentrations of Cu, Cr and As in the leachates were determined using AAS as described previously.

5.2. Results

The leaching results for the samples containing sludges without added sawdust are given in Tables 22, 23, 24 and 25 and the leaching results for samples containing added sawdust are given in Tables 26 and 27.

The leaching results of the stabilised Penrose sludge are presented in Table 22 and Fig. 13. The amounts of Cu, Cr and As added to the cement-sand matrices were calculated

from the concentration of metals in the sludge and the amount of sludge that was added. The concentrations of Cu, Cr and As in the sludge were 7200 mg/kg, 19400 mg/kg, and 28900 mg/kg respectively (Table 11). The concentrations of Cr and As in all of the leachates were less than 5 mg/L, i.e. within acceptable levels for land disposal according to current environmental guidelines (Victoria EPA, 1986). As the dilution factor (leaching solution : solid) for the TCLP test is 20, less than 0.8 % of As and 1.2 % of Cr present in the matrices were effectively leached from the samples (samples 114 and 112 respectively).

Table 22. Cu, Cr and As concentrations in the leachate from s/s Penrose sludge without the addition of sawdust

Sample	Cement:Sand: H_2O:Sludge [weight parts]	Metal addition [mg/kg]			Metal concentration in the leachate [mg/L]		
		Cu	Cr	As	Cu	Cr	As
110	1:2:0.4:0.8	1370	3600	5500	0.1	2.0	0.7
111	1:2:0.4:1.0	1640	4410	6570	0.2	0.8	2.3
112	1:2:0.4:1.2	1880	5060	7540	0.1	3.0	2.1
113	1:2:0.4:1.4	2100	5660	8430	1.0	1.7	2.2
114	1:2:0.4:1.6	2300	6210	9250	0.2	3.7	3.5
115	1:2:0.4:1.8	2490	6720	10000	0.3	2.5	3.4
116	1:2:0.4:2.0	2670	7190	10700	0.3	3.1	1.5
117	1:2:0.4:2.2	2830	7620	11350	0.2	3.2	2.1

The leaching results for stabilised Mogo sludge are shown in Table 23 and Fig. 14. The concentrations of Cu, Cr and As in the untreated sludge were 16000 mg/kg, 38500 mg/kg, and 92600 mg/kg respectively (Table 11). The amounts of Cr and As present in the cement-sand matrices were very high; up to 15130 mg/kg of Cr and 36380 mg/kg of As. The concentration of Cr in most of the TCLP leachates exceeded the acceptable levels for land disposal. High Cr concentration in the leachates probably resulted from a

high concentration of Cr(VI) (1294 mg/kg) in the Mogo sludge (Table 13). In addition 3 out of 8 leachates had a concentration of As higher then 5 mg/kg.

Table 23. Cu, Cr and As concentrations in the leachate from s/s Mogo sludge without the addition of sawdust

Sample	Cement:Sand: H_2O:Sludge [weight parts]	Metal addition [mg/kg]			Metal concentration in the leachate [mg/L]		
		Cu	Cr	As	Cu	Cr	As
118	1:2:0.4:0.8	3050	7330	17640	0.1	4.6	2.4
119	1:2:0.4:1.0	3640	8750	21050	0.2	4.2	2.4
120	1:2:0.4:1.2	4170	10040	24160	0.1	11.5	2.4
121	1:2:0.4:1.4	4670	11230	27010	0.5	11.5	4.6
122	1:2:0.4:1.6	5120	12320	29630	1.3	10.8	3.4
123	1:2:0.4:1.8	5540	13330	32050	0.2	10.7	9.2
124	1:2:0.4:2.0	5930	14260	34300	0.2	17.6	7.9
125	1:2:0.4:2.2	6290	15130	36380	5.3	16.3	7.4

The results of TCLP tests for the cement-sand matrices containing Bombala sludge are shown in Table 24 and Fig. 15. The leaching results for these samples were well below the EPA standard for disposal by landfill. The concentrations of Cr and As in all of the leachates were less than 2 mg/L and 3 mg/L respectively. Since the concentrations of Cu, Cr and As in the Bombala sludge were lower than in the other sludges treated by s/s process, 6500 mg/kg, 17600 mg/kg, and 21600 mg/kg respectively (Table 11) the amounts of Cr and As present in the cement-sand matrices were relatively small; less than 6910 mg/kg of Cr and 8490 mg/kg of As.

Table 24. Cu, Cr and As concentrations in the leachate from s/s Bombala sludge without the addition of sawdust

Sample	Cement:Sand: H_2O:Sludge [weight parts]	Metal addition [mg/kg]			Metal concentration in the leachate [mg/L]		
		Cu	Cr	As	Cu	Cr	As
126	1:2:0.4:0.8	1240	3350	4110	0.1	0.2	1.5
127	1:2:0.4:1.0	1500	4000	4910	0.1	0.4	1.3
128	1:2:0.4:1.2	1700	4600	5640	0.1	0.7	1.1
129	1:2:0.4:1.4	1800	5130	6300	0.1	0.4	1.7
130	1:2:0.4:1.6	2080	5630	6900	0.2	0.8	1.6
131	1:2:0.4:1.8	2250	6090	7480	0.2	1.9	0.6
132	1:2:0.4:2.0	2400	6520	8000	0.3	0.5	2.7
133	1:2:0.4:2.2	2550	6910	8490	0.5	0.5	1.7

The leaching results for the stabilised Hume sludge are presented in Table 25 and Fig. 16. Again the additions of Cu, Cr and As were calculated from the amount of sludge added to the cement-sand matrices. The concentrations of Cu, Cr and As in the sludge were 7600 mg/kg, 17800 mg/kg, and 23100 mg/kg respectively (Table 11). The concentrations of Cr and As in all of the leachates were within acceptable levels for land disposal.

The metal concentrations of the leachates from the cement-sand matrices containing Penrose sludge with the addition of 10% sawdust are given in Table 26 and Figures 17 and 18. These samples were very stable. For example, only 0.06 % of As from sample 150 was released into the leachate.

Table 25. Cu, Cr and As concentration in the leachate from s/s Hume sludge without the addition of sawdust

Sample	Cement:Sand: H_2O:Sludge [weight parts]	Metal addition [mg/kg]			Metal concentration in the leachate [mg/L]		
		Cu	Cr	As	Cu	Cr	As
134	1:2:0.4:0.8	1450	3390	4400	0.3	0.7	1.8
135	1:2:0.4:1.0	1730	4050	5250	0.3	1.0	0.7
136	1:2:0.4:1.2	1980	4630	6030	0.3	1.0	0.7
137	1:2:0.4:1.4	2220	5190	6740	0.5	1.1	1.5
138	1:2:0.4:1.6	2430	5700	7390	0.5	0.8	2.6
139	1:2:0.4:1.8	2630	6160	8000	0.9	2.0	2.9
140	1:2:0.4:2.0	2820	6590	8560	0.8	1.6	2.3
141	1:2:0.4:2.2	2990	6990	9080	0.8	1.2	3.7

Table 26. Cu, Cr and As concentrations in the leachate from s/s Penrose sludge with the addition of 10% of hardwood sawdust

Sample	Cement:Sand: H_2O:Sludge [weight parts]	Metal addition [mg/kg]			Metal concentration in the leachate [mg/L]		
		Cu	Cr	As	Cu	Cr	As
142	1:2:0.4:1	1490	4010	5970	0.11	0.32	0.5
143	1:2:0.4:1.5	2000	5400	8040	0.58	0.67	1.3
144	1:2:0.4:2	2430	7200	9740	0.28	0.67	1.8
145	1:1:0.4:3	3640	9800	14000	0.33	0.69	2.8
146	1:1:0.4:2	2980	8020	11940	0.24	1.21	0.6
147	1:0.5:0.3:1	2340	6300	9390	0.15	0.67	0.0
148	1:0.5:0.3:2	3450	9290	13830	0.31	1.10	0.4
149	1:0.5:0.3:3	4090	11030	16420	0.45	3.85	1.7
150	1:0:0.2:2	4090	11030	16420	0.32	2.78	0.5
151	1:0:0.2:3	4680	12600	18770	0.43	2.40	2.3

Despite the fact that the cement-sand matrices containing Mogo sludge with the addition of sawdust (Table 27) generally contained higher amounts of Cr and As than those containing the sludge without the addition of sawdust (Table 23), the leachability of the former was lower (Figures 19 and 20). Sample 161 which contained 25000 mg/kg and 60130 mg/kg of Cr and As respectively released only 1.41 mg/L of Cr and 3.2 mg/L of As into the acid leachate. Leachability of metals did not appear to be proportional to the quantity of sludge added to cement-sand matrices and poor mixing of the sludge with sand and cement may account for this.

Table 27. Cu, Cr and As concentrations in the leachate from s/s Mogo sludge with the addition of 10% of hardwood sawdust

Sample	Cement:Sand: H_2O:Sludge [weight parts]	Metal addition [mg/kg]			Metal concentration in the leachate [mg/l]		
		Cu	Cr	As	Cu	Cr	As
152	1:2:0.4:1	3310	7960	19150	0.08	0.78	1.4
153	1:2:0.4:1.5	4450	10730	25800	0.55	0.46	0.7
154	1:2:0.4:2	5390	12980	31210	2.66	1.14	1.6
155	1:1:0.4:3	8080	19450	46770	0.37	0.51	3.8
156	1:1:0.4:2	6610	15910	38270	0.17	1.24	3.0
157	1:0.5:0.3:1	5000	12500	30070	0.08	0.72	1.9
158	1:0.5:0.3:2	7660	18420	44310	0.28	1.02	2.2
159	1:0.5:0.3:3	9090	218880	52610	0.24	1.62	3.7
160	1:0:0.2:2	9090	21880	52610	0.16	1.81	3.3
161	1:0:0.2:3	10390	25000	60130	0.75	1.41	3.2

Although the initial pH of the acetic acid solutions used for the TCLP test was 2.8, the final pH of all of the solutions used to leach encapsulated sludges from commercial plants was high (Appendix J). The pH increase was probably due to the formation of calcium hydroxide which is the product of hydration reactions of cement components

(Shively *et al.,* 1986). No apparent correlation between final pH and the concentration of Cu, Cr and As in the leachates was found. Similarly the amounts of sludge and cement added to cement-sand mixes did not correlate with the pH of the leachates. The concentration of As released by some samples tended to be slightly lower if final pH of the leachate was higher than 11. However, no clear conclusion of the effect of pH on the leachability of metals from s/s samples can be drawn.

Fig. 13. Cu, Cr and As concentrations in the leachate of s/s Penrose sludge; (x sludge, 100 cement, 200 sand)

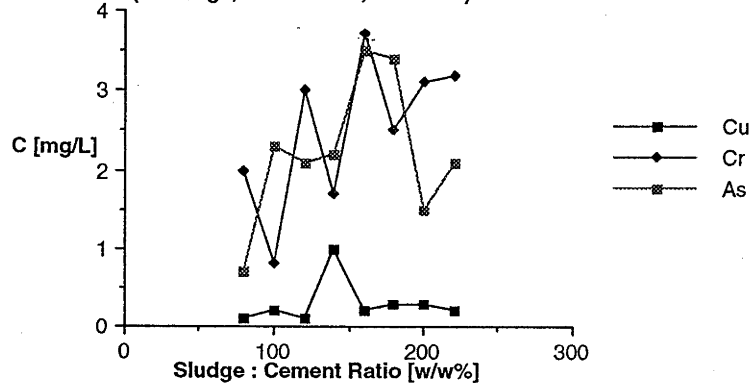


Fig. 14. Cu, Cr and As concentrations in the leachate of s/s Mogo sludge; (x sludge, 100 cement, 200 sand)

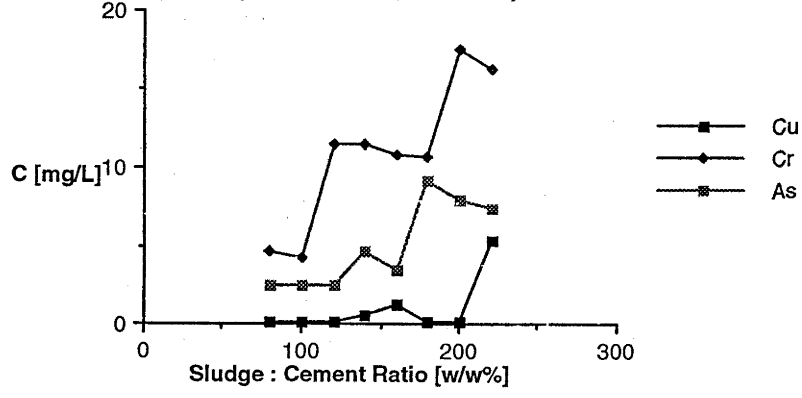


Fig. 15 Cu, Cr and As concentrations in the leachate of s/s Bombala sludge; (x sludge, 100 cement, 200 sand)

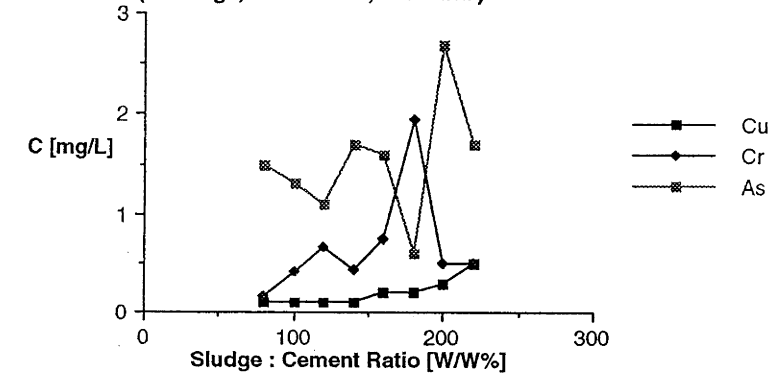


Fig. 16. Cu, Cr and As concentrations in the leachate of s/s Hume sludge; (x sludge, 100 cement, 200 sand)

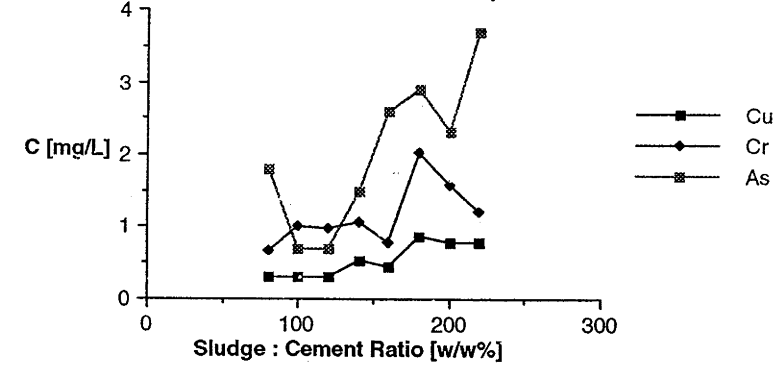


Fig. 17 Cr concentration in the leachate
of s/s Penrose sludge;
(x sludge : 100 cement : 200 sand : 0 and 10 sawdust SD)

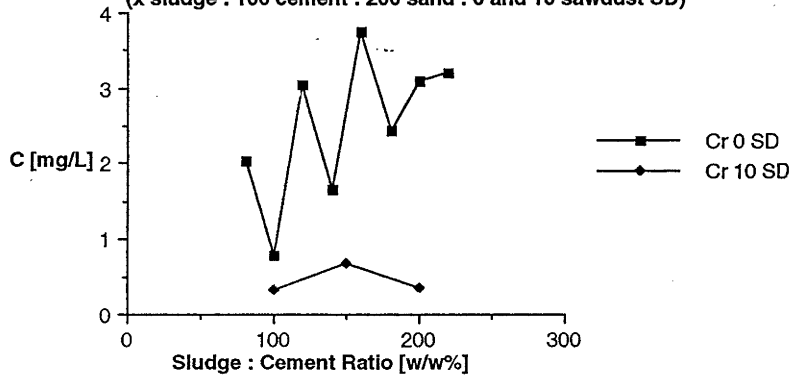


Fig. 18 As concentration in the leachate
of s/s Penrose ludge;
(x sludge, 100 cement, 200 sand, 0 and 10 sawdust SD)

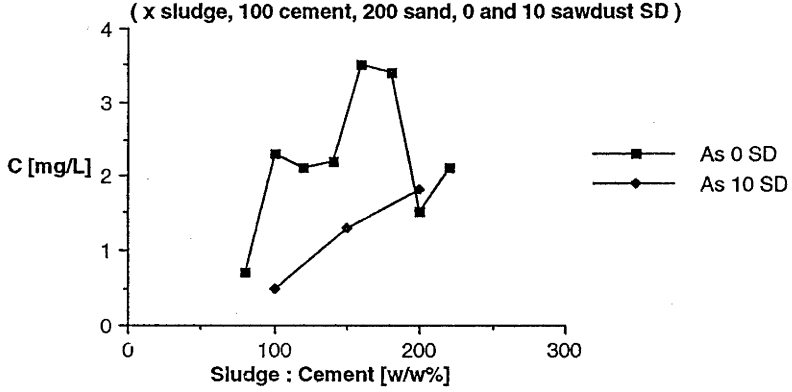


Fig. 19 Cr concentration in the leachate
of s/s Mogo sludge;
(x sludge, 100 cement, 200 sand, 0 or 10 sawdust SD)

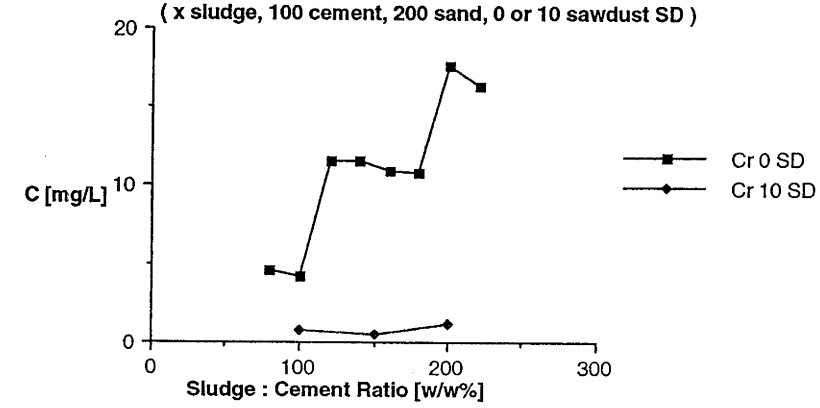
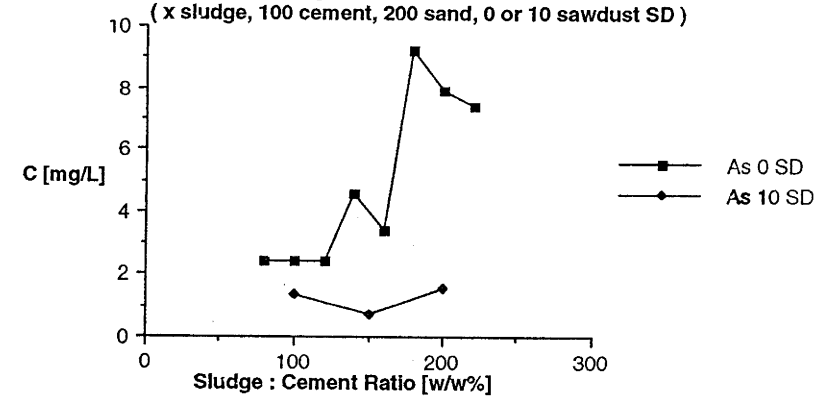


Fig. 20 As concentration in the leachate
of s/s Mogo sludge;
(x sludge, 100 cement, 200 sand, 0 or 10 sawdust SD)



Chapter 6. General discussion

The leachability of metals from CCA sludges treated using cement-based s/s method depended on a number of factors. The effect of CCA components and the interrelationships of the properties which were important for stabilisation are discussed in detail below.

6.1. Effect of sawdust treatment on the leaching of Cr and As from s/s wastes

After encapsulation untreated sludges from Penrose, Bombala and Hume met the EPA standards. The concentrations of metals in the leachates from the Penrose (Table 22, Fig. 13) samples were generally higher than for the Bombala (Table 24, Fig. 15) and Hume (Table 25, Fig. 16) samples. Most untreated Mogo samples did not meet the EPA leachate requirements for chromium, and 3 out of 8 samples did not meet the requirements for arsenic (Table 23, Fig. 14). Interestingly after the addition of sawdust s/s samples containing Mogo sludge met the EPA requirements (Table 27) .

Sawdust was effective as a reducing agent and as a material able to bind Cu-Cr-As (Appendix A, Fig. 3, Fig. 4) although the amount of sawdust added to the sludges was quite large. The average concentrations of soluble Cu, Cr and As were higher in the Mogo than in the Penrose sludge and hence the levels of sawdust needed to reduce the soluble substances in the Penrose sludge may have been less than the amount added. On the other hand, variation in the concentration of metals in the sludges was high so that fixation of active substances could only be ensured by adding an excess of sawdust.

6.2. Stabilisation of chromium in s/s forms

6.2.1. Effect of Cr(VI)

The s/s cement-sand fraction having particles smaller than 9 mm was able to retain approximately 60% of the Cr(VI) which had been added. The samples ground to a particle size smaller than 0.3 mm retained a smaller proportion of Cr (Appendix B, Fig. 6). Crushed particles containing no organic matter or soil were characterised by a high resistance to disintegration during the leaching process. We may assume that part of the Cr(VI) which was not leached by the acid solution was retained in the pores of the s/s particles. This assumption seems plausible, since Portland cement does not contain any reducing substances (Table 16). Encapsulated samples containing soil or sawdust disintegrated more readily. Thus a higher proportion of Cr(VI) is likely to be leached out of such samples since a larger surface area will be exposed to the acetic acid solution. The proportion of Cr(VI) which can be leached from samples showing poor cohesion or low compressive strength may reach 100%. Thus, to calculate the optimum formulation for the encapsulation of CCA the likelihood of disintegration has to be taken into account. On the other hand the cohesion of particles is not important if the concentration of soluble chromium compounds in the sludge is reduced through washing or the addition of sawdust prior to solidification/stabilisation.

Since the leaching of chromium from encapsulated CCA sludges appears to be dependant on the concentration of Cr(VI) in them, a formula for calculating the optimum ratio of sludge, cement, sand and water for s/s of CCA sludges can be suggested. This formula should enable one to calculate the approximate concentration of chromium that will be removed from cement-sand matrices with different compositions as a result of leaching. The formula also enables the calculation of a suitable matrix to stabilise a given sludge.

The calculation formula is designed according to the simplified (model) behaviour of CCA in cement-sand samples, which will be outlined as follows: Cement and sand are assumed, in the model, to create a benign chemical environment for Cr(VI), meaning that the chemical character of Cr(VI) is not changed by the addition of cement and sand. Solidified particles of encapsulated sludge are thus assumed to release all of the Cr(VI) into the leaching solution. The cohesion of the matrix after leaching is assumed to be zero and the matrix particles are disintegrated into tiny particles. In reality cement mixed with the sludge is able to improve the cohesion of the matrix particles, and thus reduce leaching. However, in the calculation model the worst case is considered, namely encapsulated waste after leaching releases all of the Cr(VI) into the leaching solution. The trivalent chromium compounds are regarded as insoluble in the standard acetic acid leaching solution (Table 28).

Table 28. Solubility products for some Cu, Cr and As substances

Compound	Formula	T [°C]	S_{BmAn}
Chromium arsenate	$CrAsO_4$	20	7.8×10^{-21}
Chromium hydroxide	$Cr(OH)_3$	25	1.0×10^{-17}
Cupric arsenate	$Cu_3(AsO_4)_2$	20	7.6×10^{-36}
Cupric chromate	$CuCrO_4$	25	3.6×10^{-6}
Cupric hydroxide	$Cu(OH)_2$	25	1.3×10^{-16}

S_{BmAn} - solubility product

Taking into account the outlined model behaviour of CCA sludge in cement-sand matrices the calculation formula [9] can be given as follows:

$$CF_{Cr} = \frac{C_{Cr(VI)}}{D_F \times D_E} \qquad [9]$$

$$D_F = \frac{W_{Ce} + W_{Sa} + W_{Wc} + W_{Sl}}{W_{Sl}} \qquad [10]$$

CF_{Cr}	-	the calculated concentration Cr in the leaching solution
$C_{Cr(VI)}$	-	the concentration Cr(VI) in the sludge
D_F	-	the dilution factor for the given formulation
D_E	-	the dilution factor for the leaching test, (for the standard leaching test this is 20)
W_{Ce}	-	the weight of cement in the given formulation
W_{Sa}	-	the weight of sand in the given formulation
W_{Wc}	-	the approximate weight of water consumed for the hydration of cement in a given formulation
W_{Sl}	-	the weight of sludge in a given formulation

Examples of the use of this calculation formula will be given for encapsulated sludges from various Koppers' treatment plants. For example, in sample 115 the Cr(VI) concentration in the Penrose sludge (108 mg/L, Table 13) was diluted by the addition of sand, cement and water approximately 2.89 times (D_F=2.89). Taking into account the leaching dilution factor 20(D_E=20), the concentration of Cr in the leaching solution (CF_{Cr}) should be 1.87 mg/L. Actual measurements showed it to be 2.5 mg/L. All of the leaching results for the s/s sludges from Bombala (Table 29) and Hume (Table 30) are in fairly good agreement with those predicted by the model. However, the concentrations of chromium in the leachates from the s/s Penrose sludge samples without the addition of sawdust were higher than predicted (Table 31).

Encapsulated samples containing the original Mogo sludge did not meet EPA requirements. Furthermore when using the calculation formula for this sludge the predicted concentration of soluble Cr was also too high to meet EPA requirements (Table 32). However the concentrations of Cr in the Mogo leachates was lower than predicted by the calculation formula (Table 32). The concentration of soluble Cr, $C_{Cr(VI)}$, used in the calculation was for fresh sludge. If the sludge had contained organic matter then the concentration of Cr(VI) could have been reduced significantly before encapsulation occurred. Thus the oxidation-reduction equilibrium in the sludge could have been reached later during the curing of the solidified samples. This could account for the difference in the actual Cr content of the leachate and that predicted by the formula.

The leaching results are in fairly good agreement with the predicted values. Any differences are possibly due to fluctuations in the concentration of soluble compounds in the sludges, and because organic matter present in the encapsulated sample may have fixed the soluble metals present in the sludges during curing. Sludges with the addition of sawdust were encapsulated after 15 days of fixation and the chemical reduction of CCA compounds in this system might have been reached later. Since sludge containing sawdust is not homogeneous, the absorption of soluble substances by sawdust particles might be variable. Also the fact that the cement-sand matrices contained up to 25000 mg/kg of Cr might have contributed to the fluctuation in Cr concentration of the leachates. Taking this into account the use of the relative calculation error instead of the absolute calculation error for assessing the calculation formula would not be appropriate without considering the effect of sludge components. Generally, however the leaching results are in accord with those predicted by the formula. The formula also clearly demonstrates the association of Cr leachability from s/s sludge with the presence of Cr(VI).

The formula can be converted to the form [11] which can be used to calculate the dilution factor required for a given sludge.

$$D_F = \frac{C_{Cr(VI)}}{CF_{Cr} \times D_E} \qquad [11]$$

If the concentration of soluble chromium, $C_{Cr(VI)}$, in a sludge was determined, then the dilution factor required for its satisfactory encapsulation can be calculated. The EPA requirement for the acceptable concentration of Cr in leachates is less than 5 mg/L. To ensure that encapsulated sludge will meet this limit a value of 4 or 4.5 mg/L for CF_{Cr} can be used if the sludge is homogeneous. If the sludge is not homogeneous, a value of 3 or 3.5 mg/L should be used. Since D_E is always 20 in the EPA standard leaching procedure, and assuming CF_{Cr} is for example 4, then for a sludge with a concentration of soluble Cr of 200 mg/L, the dilution factor, D_F, for the formulation will be 2.5.

The required addition of cement, sand and water can then be calculated for 100 parts of sludge using a re-arranged form of equation [10].

$$(D_F - 1) \times W_{Sl} = W_{Ce} + W_{Sa} + W_{Wc} \qquad [12]$$

$$W_{Ce} + W_{Sa} + W_{Wc} = 150 \qquad [13]$$

Thus it is necessary to add 150 parts of cement, sand and water to 100 parts of sludge with a soluble Cr concentration of 200 mg/L in order to meet the EPA requirements.

The amount of water, W_{Wc}, used in equation [13] is the approximate amount of water which is consumed by the hydration of cement and adsorbed by the samples. The amount of water needed for the formulation depends on the ratio of cement to sand. Formulations with a high cement content consume more water than those with a low cement content. Higher proportions of cement to sand improve the physical character of encapsulated sludges, and also increase the pH of the cement matrix. Sometimes it may not be necessary to add water to the sand and cement if the sludge already has a high water content. The ratio of cement to sand might be very important if physical criteria for the acceptance of solidified waste at disposal sites were introduced by the EPA.

Table 29. Predicted concentrations, $CF_{Cr(VI)}$ and determined concentrations, $M_{Cr(VI)}$ of Cr in the leachates from s/s Bombala sludge

Sample	$M_{Cr(VI)}$ [mg/L]	$CF_{Cr(VI)}$ [mg/L]	$M_{Cr(VI)}$-$CF_{Cr(VI)}$
126	0.2	0.33	-0.13
127	0.4	0.40	0.00
128	0.7	0.46	0.24
129	0.4	0.51	-0.11
130	0.8	0.56	0.24
131	1.9	0.61	1.29
132	0.5	0.65	-0.15
133	0.5	0.69	-0.19

Table 30. Predicted concentrations, $CF_{Cr(VI)}$ and determined concentrations, $M_{Cr(VI)}$ of Cr in the leachates from s/s Hume sludge

Sample	$M_{Cr(VI)}$ [mg/L]	$CF_{Cr(VI)}$ [mg/L]	$M_{Cr(VI)}$-$CF_{Cr(VI)}$
134	0.7	0.58	0.09
135	1.0	0.69	0.26
136	1.0	0.80	0.13
137	1.1	0.89	0.13
138	0.8	0.98	-0.26
139	2.0	1.06	0.86
140	1.6	1.13	0.38
141	1.2	1.20	-0.09

Table 31. Predicted concentrations, $CF_{Cr(VI)}$ and determined concentrations, $M_{Cr(VI)}$ of Cr in the leachates from s/s Penrose sludge

Sample	MCr(VI) [mg/L]	$CF_{Cr(VI)}$ [mg/L]	$M_{Cr(VI)}$-$CF_{Cr(VI)}$
110	2.0	1.03	0.97
111	0.8	1.23	-0.43
112	3.0	1.41	1.59
113	1.7	1.58	0.13
114	3.7	1.73	1.97
115	2.5	1.87	0.63
116	3.1	2.12	1.08
117	3.2	2.12	1.08

Table 32. Predicted concentrations, $CF_{Cr(VI)}$ and determined concentrations, $M_{Cr(VI)}$ of Cr in the leachates from s/s Mogo sludge

Sample	$M_{Cr(VI)}$ [mg/L]	$CF_{Cr(VI)}$ [mg/L]	$M_{Cr(VI)}$-$CF_{Cr(VI)}$
118	4.6	12.32	-7.72
119	4.2	14.70	-10.50
120	11.5	16.88	-5.38
121	11.5	18.87	-7.37
122	10.8	20.70	-9.90
123	10.7	22.40	-11.70
124	17.6	23.96	-6.36
125	16.3	25.42	-9.12

Table 33. Predicted concentrations, $CF_{Cr(VI)}$ and determined concentrations, $M_{Cr(VI)}$ of Cr in the leachates from s/s Penrose sludge with the addition of sawdust

Sample	$M_{Cr(VI)}$ [mg/L]	$CF_{Cr(VI)}$ [mg/L]	$M_{Cr(VI)}$-$CF_{Cr(VI)}$
142	0.32	0.17	0.15
143	0.67	0.23	0.44
144	0.67	0.28	0.39
145	0.69	0.35	0.34
146	1.21	0.34	0.87
147	0.67	0.27	0.40
148	1.1	0.39	0.71
149	3.85	0.47	3.38
150	2.78	0.47	2.31
151	2.4	0.54	1.86

Table 34. Predicted concentrations, $CF_{Cr(VI)}$ and determined concentrations, $M_{Cr(VI)}$ of Cr in the leachates from s/s Mogo sludge with the addition of sawdust

Sample	$M_{Cr(VI)}$ [mg/L]	$CF_{Cr(VI)}$ [mg/L]	$M_{Cr(VI)}$-$CF_{Cr(VI)}$
152	0.78	0.13	0.66
153	0.46	0.17	0.29
154	1.14	0.20	0.94
155	0.51	0.26	0.25
156	1.24	0.25	0.99
157	0.72	0.19	0.53
158	1.02	0.29	0.73
159	1.62	0.34	1.28
160	1.81	0.37	1.44
161	1.41	0.41	1.00

Since the solubility of chromium/arsenic fixation products is low (Table 28), it is essential to convert any soluble Cr and As compounds in sludge into such products prior to stabilisation/solidification processing. From the results of leaching tests (Tables 22-27) it is evident that if a sample passed the TCLP test for the concentration of Cr in leachates, it also passed the test for arsenic. We can infer from this that the stabilisation of chromium by the reduction of Cr(VI) to Cr(III) using a reducing agent probably had a similar beneficial effect on the stabilisation of As. Chromium and As may react together during fixation resulting in the formation of insoluble compounds (Table 28) and chromium might also be partly bound in the encapsulated matrix in the form of organometallic complexes (Pizzi, 1981, 1982a). In order to evaluate the ability of cement substances and cement matrices to stabilise or incorporate copper, chromium and arsenic, samples were tested which contained only pure Cu, Cr and As compounds.

When cement-sand matrices containing Cr(VI) in the concentration range 0.01-0.4 parts per 100 parts of cement and 200 parts of sand (Fig. 6) were leached using the TCLP test, the average reduction in leaching was only 60%. Thus 40% of Cr in samples containing particles of a size less than 6 mm was leached by the acid leachate. The matrix particles containing Cr(VI) showed high cohesion, and were not reduced in size during leaching. The particles less than 0.3 mm in size released about 60% of the Cr (Fig. 6) and the concentration gradient was steeper than for the particles less than 6 mm in size. It is believed that samples composed of smaller particles would show higher levels of leaching. Thus the ratio of the amount of Cr leached from samples to the amount of Cr(VI) added would be higher (Fig. 6). Therefore, we can deduce that chromium in the form of Cr(VI) was not chemically stabilised, but physically encapsulated.

Since cement substances have no reducing potential (Table 16), Cr(VI) stays in the highly soluble hexavalent state and no insoluble hydroxide or silicate chromium compounds are formed. The leachate from the solidified samples containing a significant amount of Cr(VI) had an orange colour typical of hexavalent chromic compounds. The concentration of Cr in the leachate thus depends on the size of the leached matrix particles (Fig. 6). Cr(VI) probably remains within cement pores or is loosely bound to the products of cement hydration through sorption (Poon *et al.,* 1985). The initial setting of cement does not seem to be affected by the addition of Cr(VI), i.e. the Cr(VI) cement-sand matrices were hard after 1 day of curing, but the resulting samples had a much lower compressive strength than the controls (Table 21 and Fig. 11). The adsorbed Cr(VI) might play a role in forming a weaker matrix by interrupting the bonds between the cement constituents. These findings accord with those of Tashiro *et al.* (1977) who showed that the compressive strength of concrete was very dependant on its method of preparation.

6.2.2. Effect of Cr(III)

Although cement appeared to have only a limited capability to stabilise Cr(VI), it was able to stabilise or encapsulate Cr(III) even if large quantities of a chromium (III) compound were added to the cement-sand matrices. For example, the concentration of Cr in a TCLP leachate after testing of samples containing 25800 mg/kg of Cr(III) was only 0.36 mg/L (Table 19).

The low levels of leaching of chromium and the relatively high compressive strength of samples containing Cr_2O_3 (Appendices C and G, Fig. 7 and Table 21) suggest that Cr(III) compounds are compatible with the products of cement hydration. Chromium trioxide probably precipitates as hydroxide or silicate under the alkaline conditions of cement solutions (Bishop, 1988). Thus Cr(III) may be chemically stabilised forming insoluble compounds within the cement matrix.

SEM micrographs (3-4) showed that the structure of hydrated cement after the addition of Cr(III) did not differ substantially from the hydrated cement controls (Micrographs 1-2). Although the Cr(III)-bearing cement contained more ettringite crystals, the size of crystals in both samples was similar. Again this suggests that Cr(III) does not profoundly interfere with the hydration of cement. The Cr(III)-bearing samples were set hard after 1 day of curing and the reduction in compressive strength was not as great as for samples containing other compounds (Table 21). The compressive strength of samples was strongly affected by the addition of water and the amount of water may not have been optimal for each of the cement-sand samples (Table 21), since 40 parts of water per 100 parts of cement was added to all of them.

6.3. Stabilisation of Cu in s/s forms

Results in Chapter 4 (Fig. 8) showed that cement was able to stabilise/encapsulate soluble Cu in the form of $CuSO_4.5H_2O$. The ratio of copper added to the samples and the amount leached out during the standard leaching test was negligible, around 3000. Similarly, when CCA sludges, which mostly contained copper arsenates, were added to the cement-sand matrices, the leachability of Cu from these samples was minimal. For example the concentration of Cu in TCLP leachates after testing samples containing 10390 mg/kg of Cu was only 0.75 mg/L (Table 27).

From the measurements of compressive strength (Table 21) we can conclude that the addition of Cu(II) in the form of soluble $CuSO_4.5H_2O$ to the cement-sand mixes had a significant effect on cement hydration (Micrographs 7-8). Since Cu(II) was added in the form of $CuSO_4.5H_2O$, sulphate anions probably contributed to the strength decreases. SEM observations (Micrographs 7-8) showed well-developed ettringite crystals. The crystal morphology of the cement seemed to be affected by the supply of sulphate anions added to the cement mix, since the size of the crystals was significantly smaller than those present in normal hydrated Portland cement. Also Cu(II) probably limits the crystal growth of other phases.

Leaching results showed that despite the large surface area of cement-sand particles, the concentration of copper released was small. This indicates that chemical stabilisation rather then physical encapsulation was probably responsible for the reduction in metal mobility. Copper may be chemically stabilised in cement in the form of hydroxide. Low Cu leachability might also indicate chemical bonding of Cu with the hydration products of cement. There were no problems in stabilising copper in cement-sand mixes; the Cu concentration in the leachates was always very low.

6.4. Stabilisation of As in s/s forms

Morphological observations and compressive strength measurements indicated that arsenic in the form of As_2O_3 and As_2O_5 significantly retarded the setting of Portland cement. All of the As-bearing cements samples were very fragile after 1 and 7 days of curing. The significant decrease of compressive strength of samples containing arsenic can be seen in Table 21. The low leachability of As (Fig. 9 and 10) and the low strength of As-containing samples might indicate chemical conversion of arsenic oxides to calcium arsenate, $CaAsO_4$ or calcium arsenite, $CaAsO_3$. However, the cement-sand samples containing 41200 mg/kg of As were very stable under acidic leaching during the TCLP test. The As concentration of leachates was only 0.4 mg/kg (Table 19). Thus, As in the form of chromium and copper arsenates, which are the principle components of metallic sludges, were stabilised by cement-sand matrices. However, the stabilisation of commercial sludges seemed to be a problem (Table 23), if the sludge contained a large concentration of soluble As (Appendix A).

Arsenic containing samples had a different morphology compared to controls (Micrographs 1-2). The As(V)-bearing cement did not contain any ettringite crystals which are typically found in uncontaminated hydrated controls. Indeed, the SEM micrographs showed profound effects of As(V) addition on the crystal structure of samples. The hydrated cement mixes contained round particles and small scale-like crystals. A marked difference was found between the effects of adding As(III) or As (V) to cement. The As(III)-containing cement (Micrograph 9 and 10) contained needle-like structures, but any crystals present were not surrounded by voids like those present in uncontaminated samples. It can be seen that As(V) retarded the crystal growth more than As(III) and the other cations Cr(III), Cr(VI) and Cu(II)) examined.

The use of ground crystal As_2O_3 instead of the dissolved form to prepare samples may have caused uneven distribution of particles within the cement-sand matrices. This in addition to its effects on the hydration might to some extent explain the decreases in compressive strength (Table 21) and changes in crystal morphology that were observed in samples containing arsenic. Since As significantly affects the hydration of cement there might be a relationship between the structural changes induced in cement by arsenic and the leachability of As from cement-based wastes. Arsenic leaching from the samples containing As in the range of 0.02-0.4 parts to 100 parts of cement was well below 1 mg/L. Tashiro *et al.* (1977) also observed very low levels of arsenic leaching from concretes containing As_2O_3. Despite the fact that both pure arsenic oxides were stabilised so effectively in cement-sand mixes (Fig. 9 and 10), the leachability of As from sludge was rather unpredictable.

The fixation mechanism and solubility of As can be dependant on several factors such as chemical species present, pH, redox potential and also the presence of admixtures able to immobilise As by sorption. De Groot *et al.* (1989) found a relationship between As leachability and the pH of fly-ash water mixtures. They concluded that pH was the main factor controlling As solubility. Decreases in the leachability of As was pronounced in the pH range 11-12 .

Dusing *et al.* (1992) studied the effect of redox potential on the leaching of metals from solidified/stabilised fly/ash and flue gas desulphurisation sludge wastes. They concluded that chromium leachability increased significantly under oxidising conditions. On the other hand arsenic leachability increased under reducing conditions. In these experiments, the addition of sawdust to reduce Cr(VI) might have affected As solubility. Though the reducing effect of sawdust is probably confined largely to the interface of the sawdust particle-cement gel, this may have increased As solubility. Despite these

interactions all of the samples which were pretreated by the addition of sawdust prior to solidification/stabilisation treatment performed satisfactorily and met the environmental requirements. Because of the ambiguous behaviour of As in cement-based solidified wastes, further morphological observations and detailed X-ray diffraction studies would be useful in determining the fixation mechanism of arsenic within cement-sand matrices.

Chapter 7. Conclusions and Recommendations

1. CCA sludges from timber treatment plants had different chemical compositions and pH. The concentrations of Cu, Cr and As varied in the range 0.7-3.5 w/w%, 1.8-19.3 w/w% and 2.2-27.6 w/w% respectively. Sludges had mildly acidic or neutral character with pH from 2.6 to 6.1. Most of the sludges contained significant amounts of extraneous materials such as soil and wood. The laboratory manufactured synthetic sludge differed significantly from the commercial plant sludges since it did not contain extraneous materials.

2. Synthetic CCA sludge free of soluble copper, chromium and arsenic compounds when stabilised in a cement-sand matrix was stable in an acetic acid solution. The leaching of Cu, Cr and As from such samples was below the regulatory limits defined by the TCLP test. Thus $CrAsO_4$, $CuCrO_4$, $Cu_3(AsO_4)_2$, $Cr(OH)_3$ and $Cu(OH)_2$ which are the principal components of synthetic CCA sludge were stable in the high pH environment of cement gels.

3. If the concentrations of water-soluble Cr and As in the contaminated waste from timber treatment plants were usually higher than 150 mg/L then the leaching of Cr and As from such cement-stabilised waste may be higher than the regulatory limits for disposal at landfill.

4. The concentrations of soluble Cr and As in some sludges can be significantly reduced by the addition of hardwood sawdust. Such cement-stabilised CCA waste meets the regulatory requirements for landfill disposal.

5. The leachability of chromium from cement-stabilised CCA waste was proportional to the concentration of soluble chromium (CrVI) in the untreated waste. However, pure

soluble copper and arsenic compounds were safely contained within cement-sand matrices up to concentrations of 7200 mg/kg and 1050 mg/kg respectively.

6. The compressive strength of cement-sand matrices with the addition of CCA sludge containing copper chromates and copper and chromium arsenates was not significantly reduced in comparison to samples containing pure copper sulphate and arsenic(III) oxide or arsenic(V) oxide. Furthermore the addition of pure chromium(III) oxide and chromium(VI) oxide had less pronounced effects on the structure of cement than pure copper and arsenic oxides.

To minimise the environmental effects of CCA waste disposal the following recommendations are made:

1. Washing of CCA contaminated waste before cement treatment and reuse of the wash water in the timber treatment process.

2. Investigations of the long-term stability of CCA waste treated by the addition of sawdust and subsequent cement stabilisation/solidification process should be undertaken.

3. Investigation of the environmental stability of CCA contaminated soil at timber treatment plants, particularly with regard to the local chemical environment should be undertaken.

4. Further research to quantify the effect of sand and other additives on the performance of cement-based CCA waste should be undertaken. Further research is also needed to determine the mechanisms of stabilisation of the various components of CCA sludge in cement matrices.

5. The use of other cheap reducing agents for pretreatment of CCA sludge should be investigated.

6. Timber treatment plants should make changes in operation and their design to minimise sludge formation and to prevent high amounts of extraneous material entering sludge.

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9. Appendices

Appendix A. Concentrations of soluble Cu, Cr and As in the CCA sludges from Bombala, Hume, Penrose and Mogo plants after the addition of sawdust and water

Sludge	Sawdust [w/w%]	Cr [mg/kg]	As [mg/kg]	Cu [mg/kg]
Bombala	0	35	47	42
Hume	0	61	68	17
Penrose	0	108	63	42
Penrose	10	15	57	40
Penrose	20	9	58	32
Mogo	0	1294	904	866
Mogo	10	11	139	201
Mogo	20	8	58	150

Appendix B. Concentration of Cr in the leachates (TCLP) from cement-sand samples with the addition of Cr(VI); Frac 1 - particles smaller than 6 mm, Frac 2 - particles smaller than 0.3 mm

Sample	Cement:Sand H_2O [Weight parts]	Cr(VI) in the sample [mg/kg]	Cr in the leachate (Frac1)[mg/L]	Cr in the leachate (Frac2)[mg/L]
1	1:2:0.45	60	1.10	1.92
2	1:2:0.45	150	2.78	4.81
3	1:2:0.45	300	5.92	7.53
4	1:2:0.45	450	6.39	14.37
5	1:2:0.45	600	8.49	17.85
6	1:2:0.45	750	9.14	22.94
7	1:2:0.45	900	17.06	32.85
8	1:2:0.45	1050	22.46	35.65

Appendix C. Concentration of Cr in the leachates (TCLP) from cement-sand samples with the addition of Cr(III)

Sample	Cement:Sand: H_2O [Weight parts]	Cr(III) in the concrete [mg/kg]	Cr in the leachate [mg/L]
1	1:2:0.45	60	0.18
2	1:2:0.45	150	0.17
3	1:2:0.45	300	0.16
4	1:2:0.45	450	0.16
5	1:2:0.45	600	0.14
6	1:2:0.45	750	0.18
7	1:2:0.45	900	0.17
8	1:2:0.45	1050	0.15

Appendix D. Concentration of Cu in the leachates (TCLP) from cement-sand samples with the addition of Cu(II)

Sample	Cement:Sand: H_2O [Weight parts]	Cu(II) in the sample [mg/kg]	Cu in the leachate [mg/L]
1	1:2:0.45	1200	0.1
2	1:2:0.45	1800	0.2
3	1:2:0.45	2400	0.4
4	1:2:0.45	3000	0.1
5	1:2:0.45	3600	0.1
6	1:2:0.45	4800	0.2
7	1:2:0.45	6000	0.2
8	1:2:0.45	7200	0.1

Appendix E. Concentration of As in the leachates (TCLP) from cement-sand samples with the addition of As(III)

Sample	Cement:Sand: H_2O [Weight parts]	As(III) in the sample [mg/kg]	As in the leachate [mg/L]
1	1:2:0.45	60	0.4
2	1:2:0.45	150	0.5
3	1:2:0.45	300	0.5
4	1:2:0.45	450	0.5
5	1:2:0.45	600	0.6
6	1:2:0.45	750	0.5
7	1:2:0.45	900	0.6
8	1:2:0.45	1050	0.6

Appendix F. Concentration of As in the leachates (TCLP) from cement-sand samples with the addition of As(V)

Sample	Cement:Sand: H_2O [Weight parts]	As(V) in the sample [mg/kg]	As in the leachate [mg/L]
1	1:2:0.45	60	0.7
2	1:2:0.45	150	0.3
3	1:2:0.45	300	0.5
4	1:2:0.45	450	0.2
5	1:2:0.45	600	0.2
6	1:2:0.45	750	0.5
7	1:2:0.45	900	0.5
8	1:2:0.45	1050	0.4

Appendix G. Compressive strength of the samples containing synthetic sludge the addition of water 0. 4 parts per 1 part of cement

Sample	Cement:Sand: H_2O: Sludge [weight parts]	Metal addition [mg/kg]			Compressive Strength [N/cm^2]
		Cu	Cr	As	
1	1:2:0.4:0	0	0	0	4330
2	1:2:0.4:0.02	430	940	1860	3260
3	1:2:0.4:0.04	860	1870	3690	2740
4	1:2:0.4:0.06	1290	2790	5510	4820
5	1:2:0.4:0.09	1910	4140	8190	4830
6	1:2:0.4:0.12	2530	5480	10820	4390

Appendix H. Compressive strength of the samples containing synthetic sludge; the addition of water 0. 5 parts per 1 part of cement

Sample	Cement:Sand: H_2O: Sludge [weight parts]	Metal addition [mg/kg]			Compressive Strength [N/cm^2]
		Cu	Cr	As	
1	1:2:0.5:0	0	0	0	2340
2	1:2:0.5:0.02	420	910	1800	1900
3	1:2:0.5:0.04	840	1820	3590	1750
4	1:2:0.5:0.06	1250	2710	5350	2190
5	1:2:0.5:0.09	1860	4030	7960	2970
6	1:2:0.5:0.12	2460	5330	10520	2740

Appendix I. Compressive strength of samples containing Narangba sludge

Sample	Cement:Sand: H_2O: sludge [weight parts]	Metal addition [mg/kg]			Compressive Strength [N/cm^2]
		Cu	Cr	As	
1	1:2:0.5:0	0	0	0	2340
2	1:2:0.5:0.04	390	1850	2960	2390
3	1:2:0.5:0.06	590	2760	5400	2860
4	1:2:0.5:0.09	870	4110	6570	2360
5	1:2:0.5:0.12	1150	5440	8680	2210
6	1:2:0.5:0.15	1430	6740	10760	2860
7	1:2:0.5:0.2	1880	8860	14160	2470
8	1:2:0.5:0.3	2750	12950	20680	2840
9	1:2:0.6:0.4	3480	16400	26190	2560
10	1:2:0.7:0.5	4140	19520	31180	1060
11	1:2:0.7:0.6	4860	22880	36500	1770
12	1:2:0.75:0.7	5470	25800	41200	1290

Appendix J. pH of the TCLP leachates from s/s samples containing sludge from commercial treatment plants

Sample	pH	Sample	pH	Sample	pH
110	11.1	128	11.8	146	12.0
111	10.4	129	11.2	147	13.1
112	11.5	130	11.6	148	12.2
113	11.1	131	11.5	149	11.4
114	10.8	132	11.3	150	12.5
115	10.5	133	11.4	151	11.2
116	9.5	134	12.3	152	8.1
117	8.1	135	12.3	153	10.1
118	10.7	136	12.4	154	10.7
119	8.0	137	8.7	155	10.4
120	8.1	138	8.2	156	10.1
121	8.2	139	10.3	157	10.7
122	10.2	140	10.7	158	9.7
123	8.3	141	8.3	159	8.7
124	9.5	142	11.9	160	8.2
125	9.0	143	12.0	161	8.4
126	12.3	144	8.2		
127	9.7	145	8.3		